Tierra Solutions, Inc.

Focused Sediment Investigation Work Plan

Quality Assurance Project Plan

Lower Passaic River Study Area

August 2011

Revision 0

TABLE OF CONTENTS

Figures:

List of Appendices:

QAPP Worksheet #1
Title and Approval Page

Site Name/Project Name: Lower Passaic River Study Area/Focused Sediment Investigation Work Plan

Site Location: Lower Passaic River Study Area, Newark, New Jersey

Document Title: Quality Assurance Project Plan

Lead Organization: Tierra Solutions, Inc. on behalf of Occidental Chemical Corporation

Preparer's Name and Organizational Affiliation: Richard J. Wenning, ENVIRON International Corporation

Preparer's Address: 6001 Shellmound Street, Suite 700, Emeryville, CA

Telephone Number: 510-420-2556

E-mail Address: rjwenning@environcorp.com

Preparation Date (Day/Month/Year): 08/12/2011

Investigative Organization's Project Coordinator: _____

Signature

Richard J. Wenning/ENVIRON International Corporation/8/12/11

Printed Name/Organization/Date

Investigative Organization's Project Manager: _____

Signature

Linda Hall/ENVIRON International Corporation/8/12/11

Printed Name/Organization/Date

Project Quality Assurance Coordinator: _____

Signature

Diane Waldschmidt/Environmental Data Services, Ltd./8/12/11

Printed Name/Organization/Date

Document Control Number: FSIWP/QAPP - Revision 0

QAPP Worksheet #2
QAPP Identifying Information

Site Name/Project Name:	Lower Passaic River Study Area/Focused Sediment Investigation Work Plan
Site Location:	Lower Passaic River Study Area, Newark, New Jersey
Site Number/Code:	Not Applicable
Operable Unit:	Not Applicable
Contractor Name:	Not Applicable
Contractor Number:	Not Applicable
Contract Title:	Not Applicable
Work Assignment Number:	Not Applicable

1. **Identify guidance used to prepare QAPP:** *Uniform Federal Policy for Quality Assurance Project Plans; Evaluating, Assessing and Documenting Environmental Data Collection and Use Programs.* U.S. Environmental Protection Agency (USEPA) Publication Number EPA-505-B-04-900C (Intergovernmental Data Quality Task Force 2005).

2. **Identify regulatory program:** Not Applicable

3. **Identify approval entity:** Not Applicable

4. Indicate whether the Quality Assurance Project Plan (QAPP) is a generic or a project-specific QAPP (Circle one).

5. **List dates of scoping sessions that were held:** Various

6. **List dates and titles of documents written for previous site work, if applicable**: None.

7. **List organizational partners (stakeholders) and connection with lead organization:** None.

8. **List data users:** see Worksheet #11.

9. **If any required QAPP elements and required information are not applicable to the project, then circle the omitted QAPP elements and required information on the attached table. Provide an explanation for their exclusion below:** None.

QAPP Worksheet #2
QAPP Identifying Information

QAPP elements and required information that are not applicable to the project are circled and an explanation is provided in the QAPP.

Required QAPP Element(s) and Corresponding QAPP Section(s)		Required Information	QAPP Worksheet # or Crosswalk to Related Document
Project Management and Objectives			
2.1	Title and Approval Page	- Title and Approval Page	1
2.2 2.2.1 2.2.2 2.2.3 2.2.4	Document Format and Table of Contents Document Control Format Document Control Numbering System Table of Contents QAPP Identifying Information	- Table of Contents - QAPP Identifying Information	2
2.3 2.3.1 2.3.2	Distribution List and Project Personnel Sign-Off Sheet Distribution List Project Personnel Sign-Off Sheet	- Distribution List - Project Personnel Sign-Off Sheet	3 4
2.4 2.4.1 2.4.2 2.4.3 2.4.4	Project Organization Project Organizational Chart Communication Pathways Personnel Responsibilities and Qualifications Special Training Requirements and Certification	- Project Organizational Chart - Communication Pathways - Personnel Responsibilities and Qualifications Table - Special Personnel Training Requirements Table	5 6 7 8
2.5 2.5.1 2.5.2	Project Planning/Problem Definition Project Planning (Scoping) Problem Definition, Site History, and Background	- Project Planning Session Documentation (including Data Needs tables) - Project Scoping Session Participants Sheet - Problem Definition, Site History, and Background - Site Maps (historical and present)	9 10
2.6 2.6.1 2.6.2	Project Quality Objectives and Measurement Performance Criteria Development of Project Quality Objectives Using the Systematic Planning Process Measurement Performance Criteria	- Site-Specific PQOs - Measurement Performance Criteria Table	11 12

QAPP Worksheet #2
QAPP Identifying Information

QAPP elements and required information that are not applicable to the project are circled and an explanation is provided in the QAPP.

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Document
Project Management and Objectives		
2.7 Secondary Data Evaluation	- Sources of Secondary Data and Information - Secondary Data Criteria and Limitations Table	13
2.8 Project Overview and Schedule 2.8.1 Project Overview 2.8.2 Project Schedule	- Summary of Project Tasks - Reference Limits and Evaluation Table - Project Schedule/Timeline Table	14 15 16
Measurement/Data Acquisition		
3.1 Sampling Tasks 3.1.1 Sampling Process Design and Rationale 3.1.2 Sampling Procedures and Requirements 3.1.2.1 Sampling Collection Procedures 3.1.2.2 Sample Containers, Volume, and Preservation 3.1.2.3 Equipment/Sample Containers Cleaning and Decontamination Procedures 3.1.2.4 Field Equipment Calibration, Maintenance, Testing, and Inspection Procedures 3.1.2.5 Supply Inspection and Acceptance Procedures 3.1.2.6 Field Documentation Procedures	- Sampling Design and Rationale - Sample Location Map - Sampling Locations and Methods/ SOP Requirements Table - Analytical Methods/SOP Requirements Table - Field Quality Control Sample Summary Table - Sampling SOPs - Project Sampling SOP References Table - Field Equipment Calibration, Maintenance, Testing, and Inspection Table	17 18 19 20 21 22

QAPP Worksheet #2
QAPP Identifying Information

QAPP elements and required information that are not applicable to the project are circled and an explanation is provided in the QAPP.

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Document
Measurement/Data Acquisition		
3.2 Analytical Tasks 3.2.1 Analytical SOPs 3.2.2 Analytical Instrument Calibration Procedures 3.2.3 Analytical Instrument and Equipment Maintenance, Testing, and Inspection Procedures 3.2.4 Analytical Supply Inspection and Acceptance Procedures	- Analytical SOPs - Analytical SOP References Table - Analytical Instrument Calibration Table - Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table	23 24 25
3.3 Sample Collection Documentation, Handling, Tracking, and Custody Procedures 3.3.1 Sample Collection Documentation 3.3.2 Sample Handling and Tracking System 3.3.3 Sample Custody	- Sample Collection Documentation Handling, Tracking, and Custody SOPs - Sample Container Identification - Sample Handling Flow Diagram - Example Chain-of-Custody Form and Seal	26 27
3.4 Quality Control Samples 3.4.1 Sampling Quality Control Samples 3.4.2 Analytical Quality Control Samples	- QC Samples Table - Screening/Confirmatory Analysis Decision Tree	28
3.5 Data Management Tasks 3.5.1 Project Documentation and Records 3.5.2 Data Package Deliverables 3.5.3 Data Reporting Formats 3.5.4 Data Handling and Management 3.5.5 Data Tracking and Control	- Project Documents and Records Table - Analytical Services Table - Data Management SOPs	29 30

QAPP Worksheet #2
QAPP Identifying Information (Continued)

QAPP elements and required information that are not applicable to the project are circled and an explanation is provided in the QAPP.

Required QAPP Elements and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Document
Assessment/Oversight		
4.1 Assessments and Response Actions 4.1.1 Planned Assessments 4.1.2 Assessment Findings and Corrective Action Responses	- Assessments and Response Actions - Planned Project Assessments Table - Audit Checklists - Assessment Findings and Corrective Action Responses Table	31 32
4.2 QA Management Reports	- QA Management Reports Table	33
4.3 Final Project Report		16 and 33
Data Review		
5.1 Overview		
5.2 Data Review Steps 5.2.1 Step I: Verification 5.2.2 Step II: Validation 5.2.2.1 Step IIa Validation Activities 5.2.2.2 Step IIb Validation Activities 5.2.3 Step III: Usability Assessment 5.2.3.1 Data Limitations and Actions from Usability Assessment 5.2.3.2 Activities	- Verification (Step I) Process Table - Validation (Steps IIa and IIb) Process Table - Validation (Steps IIa and IIb) Summary Table - Usability Assessment	34 35 36 37

QAPP Worksheet #3
Distribution List

QAPP Recipients	Title	Organization	Telephone Number	Fax Number	E-mail Address	Document Control Number
Paul Brzozowski	Project Coordinator	Tierra Solutions Inc.	(732) 246-5851	(732) 246-5858	Paul.brzozowski@tierra-inc.com	FSIWP/QAPP Revision -0
Cliff Firstenberg	Sr. Technical Advisor	Firstenberg Consulting, LLC	(757) 258-7720	(757) 208-0180	cefirstenberg@cox.net	FSIWP/QAPP Revision -0
Linda Hall	Investigative Organization's Project Manager	ENVIRON International Corporation	(510) 420-2583		lhall@environcorp.com	FSIWP/QAPP Revision -0
Richard J. Wenning	Investigative Organization's Project Coordinator	ENVIRON International Corporation	(510) 420-2556		rjwenning@environcorp.com	FSIWP/QAPP Revision -0
John Pekala	Investigative Organization's Field Team Leader	ENVIRON International Corporation	(602) 734-7700		jpekala@environcorp.com	FSIWP/QAPP Revision -0

QAPP Worksheet #3
Distribution List (Continued)

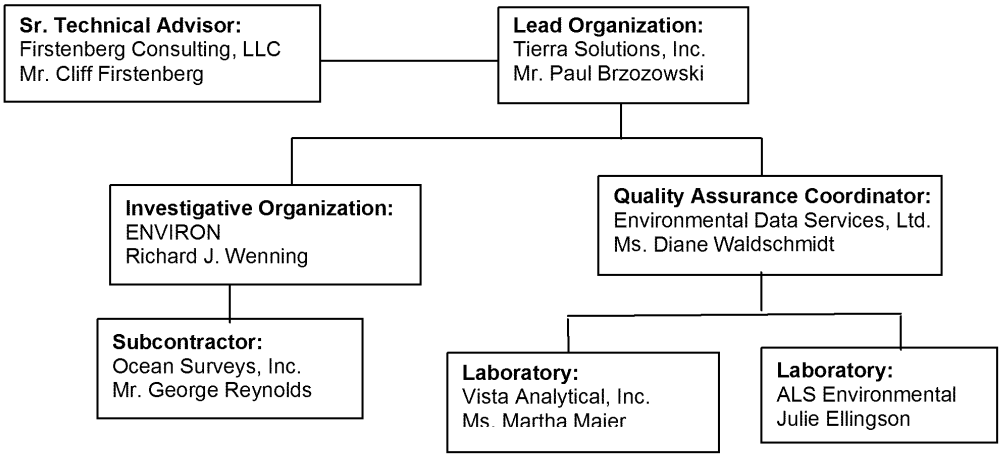
QAPP Recipients	Title	Organization	Telephone Number	Fax Number	E-mail Address	Document Control Number
Robert Adams	Investigative Organization's Health and Safety Coordinator	ENVIRON International Corporation	(609) 243-9848		radams@environcorp.com	FSIWP/QAPP Revision -0
Martha Maier	Laboratory Project Manager	Vista Analytical Laboratory	(916) 673-1520	(916) 673-0106	mmaier@vista-analytical.com	FSIWP/QAPP Revision -0
Julie Ellingson	Laboratory Project Manager	ALS Environmental	(970) 490-1511 ext. 241	(970) 490-1522	Julie.Ellingson@ALSGlobal.com	FSIWP/QAPP Revision -0
Diane Waldschmidt	Project Quality Assurance Coordinator	Environmental Data Services, Ltd.	(412) 486-6989		edatas@aol.com	FSIWP/QAPP Revision -0
Amy Kephart	On-Site Health and Safety Coordinator	ENVIRON International Corporation	(703) 516-2375		akephart@environcorp.com	FSIWP/QAPP Revision -0

QAPP Worksheet #4
Project Personnel Sign-Off Sheet

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Paul Brzozowski	Project Coordinator	(732) 246-5851		
Cliff Firstenberg	Sr. Technical Advisor	(757) 258-7720		
Linda Hall	Investigative Organization's Project Manager	(510) 420-2583		
Richard J. Wenning	Investigative Organization's Project Coordinator	(510) 420-2556		
John Pekala	Investigative Organization's Field Team Leader	(602) 734-7700		
Robert Adams	Investigative Organization's Health and Safety Coordinator	(609) 243-9848		
Martha Maier	Laboratory Project Manager	(916) 673-1520		
Julie Ellingson	Laboratory Project Manager	(970) 490-1511 ext. 241		
Diane Waldschmidt	Project Quality Assurance Coordinator	(412) 486-6989		
Amy Kephart	On-Site Health and Safety Coordinator	(703) 516-2375		

Notes:
A complete sign-off sheet will be maintained in the files.
*Signature indicates the personnel have read the applicable Quality Assurance Project Plan sections and will perform the tasks described.

QAPP Worksheet #5
Project Organizational Chart



QAPP Worksheet #6
Communication Pathways

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (e.g., Timing, Pathways)
Project reporting activities with Tierra Solutions, Inc. Investigative Organization's Project Manager	ENVIRON Project Manager	Linda Hall	510- 420-2583	Linda Hall will be ENVIRON's liaison to Paul Brzozowski.
QAPP changes in the field, manage field sample collection activities	ENVIRON Field Team Leader	John Pekala	602- 734-7700	John Pekala will notify, via e-mail, Linda Hall and Diane Waldschmidt of non-conformance and suggested corrective actions within 1 business day of identification.
Daily field progress reports	ENVIRON Field Team Leader	John Pekala	602- 734-7700	Field Team Leader will e-mail daily field progress reports to Linda Hall.
Identification of field corrective action	ENVIRON. Field Team Leader/Quality Assurance Coordinator	John Pekala	602- 734-7700	Field Team Leader, John Pekala will notify Linda Hall and Diane Waldschmidt, via e-mail, phone or face to face of non-conformance and suggested corrective action within 1 business day of identification.
Stop Work Authority	ENVIRON Field Team Leader	John Pekala	602- 734-7700	Field Team Leader will notify Linda Hall if field conditions arise that may compromise the safety of the field team and/or subcontractors on site. If such conditions exist the Field Team Leader will contact Robert Adams by phone. Robert Adams will then provide mitigation measures immediately to the Field Team Leader. Robert Adams will then notify Linda Hall. If imminent danger arises, the Field Team Leader will follow the protocols of the Health and Safety Plan.

QAPP Worksheet #6
Communication Pathways (Continued)

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (e.g., Timing, Pathways)
Reporting laboratory data quality issues	Vista Analytical, Inc. Laboratory Project Manager	Martha Maier	916- 673-1520	Quality assurance/quality control (QA/QC) issues with project field samples will be reported by Laboratory Project Manager to Diane Waldschmidt within 1 business day of identification.
Reporting laboratory data quality issues	ALS Environmental Laboratory Project Manager	Julie Ellingson	970- 490-1511 ext. 241	QA/QC issues with project field samples will be reported by Laboratory Project Manager to Diane Waldschmidt within 1 business day of identification.
Field and analytical corrective actions	Environmental Data Services, Ltd. Quality Assurance Coordinator	Diane Waldschmidt	412-486-6989	Requested field or laboratory corrective action will be evaluated and documented by Diane Waldschmidt.
Release of analytical data	Environmental Data Services, Ltd. Quality Assurance Coordinator	Diane Waldschmidt	412-486-6989	Upon approval of its release by Diane Waldschmidt, final validated data will be forwarded to Tierra Solutions, Inc. in an agreed upon format (e.g., compact disc).
QAPP amendments	Tierra Solutions, Inc.	Paul Brzozowski	609- 951-9208	Any changes requested by Linda Hall or Diane Waldschmidt must be approved by Paul Brzozowski before changes can be implemented.
Response to data requests	ENVIRON Project Manager	Linda Hall	510- 420-2583	Any request for information will be directed to the ENVIRON project manager. Under no circumstance will ENVIRON or its subcontractors disseminate information to anyone outside of the project team without the express written permission of the ENVIRON project manager

QAPP Worksheet #7
Personnel Responsibilities and Qualifications

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Paul Brzozowski	Project Manager	Tierra Solutions, Inc.	Project Coordinator	BS Civil Engineering / 25 years
Richard J. Wenning	Project Coordinator	ENVIRON International Corporation	Investigative Organization's Project Coordinator	MEM Ecotoxicology / 24 years
Linda Hall	Project Manager	ENVIRON International Corporation	Investigative Organization's Project Manager	PhD Ecological Toxicology / 25 years
John Pekala	Field Team Leader	ENVIRON International Corporation	Investigative Organization's Field Team Leader	MS Geology / 13 years
Robert Adams	Health and Safety Coordinator	ENVIRON International Corporation	Investigative Organization's Health and Safety Coordinator	MS Safety Sciences / 28 years
Julie Ellingson	Laboratory Manager	ALS Environmental	Laboratory Project Manager	BS Horticulture / 2 years
Martha Maier	Laboratory Manager	Vista Analytical Laboratory	Laboratory Project Manager	BS Chemistry / 23 years
Diane Waldschmidt	Director	Environmental Data Services, Ltd.	Quality Assurance Contractor	BS Chemistry / 22 years
Amy Kephart	Safety Coordinator	ENVIRON International Corporation	On-Site Heath and Safety Coordinator	MS Environmental Geological Sciences / 6 years

QAPP Worksheet #8
Special Personnel Training Requirements

All field personnel assigned to the site must have successfully completed 40 hours of training for hazardous site work in accordance with Occupational Safety and Health Administration (OSHA) 29 Code of Federal Regulations (CFR) 1910.120(e)(3) and be current with their 8-hour refresher training in accordance with OSHA 29 CFR 1910.120(e)(8). Documentation of OSHA training is required prior to personnel being permitted to work on site.

Personnel managing or supervising work on site will also have successfully completed 8 hours of Manager/Supervisor Training in accordance with OSHA 29 CFR1910.120(e)(4).

Personnel assigned to the site must be enrolled in a medical surveillance program, which meets the requirements of OSHA 29 CFR 1910.120(f). Personnel must have successfully passed a periodic occupational physical and be medically cleared to work on a hazardous waste site, and capable of wearing appropriate personal protective equipment and respiratory protection, as may be required. For employees potentially exposed more than 30 days per year, the frequency of periodic examinations will be annual. For employees potentially exposed less than 30 days per year, the frequency for periodic examinations will be once every 24 months.

Personnel assigned to the site who must wear a respirator must be familiar with the requirements in the OSHA respiratory standard (29 CFR 1910.134). Personnel who are required to wear respirator protection must have successfully passed a respirator fit test within the last 12 months.

It is the responsibility of the site worker's employer to provide their employees with the required training, medical monitoring, and fit testing prior to assigning them to work at the site. Each employer will be responsible for providing documentation of training, monitoring, and fit testing (with make/model of respirator) to the Field Supervisor prior to sending their employees to the site to work.

Personnel who may work in the area of potential confined spaces will be trained in awareness level training to recognize confined spaces and to understand the hazards associated with these spaces. If entry to confined spaces is required, training will be provided to the entry supervisor, attendants, and entrants, as appropriate, to the performance of activities. Specific training requirements and procedures for entry to confined spaces are detailed in the project-specific Health and Safety Plan (HASP).

Additional health and safety information and records documentation information are detailed in the project-specific HASP.

QAPP Worksheet #9
Project Scoping Session Participants Sheet

Project Name: Lower Passaic River Study Area/Focused Sediment Investigation Work Plan **Site Name:** Lower Passaic River Study Area
Projected Date(s) of Sampling: August 19, 2011 **Site Location:** Lower Passaic River Study Area, Newark, NJ
Project Coordinator: Linda Hall
Date of Session: June 3, 2011, June 6, 2011, June 20, 2011, June 23, 2011, June 27, 2011, July 18, 2011, July 27, 2011, August 1, 2011
Scoping Session Purpose: Quality Assurance Project Plan (QAPP) Planning for Focused Sediment Investigation Work Plan.
Scoping Session Outcome: The participants discussed the requirements and path forward developing and finalizing this FSIWP/QAPP. During the scoping sessions, the following items were discussed to work towards completion of the QAPP.

1. Analytes of interest: PCDDs/PCDFs, HCX and Cs-137
2. HCX method development: Vista Analytical
3. Sample locations: High priority and secondary locations
4. Equipment for core extraction, size of core and number of samples per core
5. Collection procedures and storage of cores
6. Expenditures for entire project

QAPP Recipients	Title	Organization	Telephone Number	Scoping Session Dates Participated	Project Role
Paul Brzozowski	Project Manager	Tierra Solutions, Inc.	732-246-5851	6/3, 6/6, 6/20, 6/23, 7/27	Lead Organization's Project Coordinator
Linda Hall	Project Manager	ENVIRON	510-420-2583	6/3, 6/6, 6/20, 6/23, 6/27, 7/18, 7/27, 8/1	Investigative Organization's Project Manager
Michael Potts	Project Manager	ENVIRON	609-951-9028	6/3, 6/6, 6/20, 6/23, 7/18, 7/27, 8/1	Investigative Organization's Project Manager
Diane Waldschmidt	Director	Environmental Data Services, Inc.	412-486-6989	6/3, 6/6, 6/20, 6/23, 6/27, 7/18, 7/27, 8/1	Quality Assurance Coordinator
Elise Francken	Assistant	Environmental Data Services, Inc.	412-486-6989	6/3, 6/6, 6/20, 6/23, 6/27, 7/18, 7/27, 8/1	Assistant Quality Assurance Coordinator
Jim Moran	Quality Assurance Coordinator	ENVIRON	609-243-9881	6/6, 6/27, 7/18, 7/27, 8/1	Investigative Organization's Quality Assurance Coordinator
Cliff Firstenberg	Sr. Technical Advisor	Firstenberg Consulting, LLC	757-258-7720	6/20, 6/23,	Lead Organization's Consultant
Michael Bock	Technical Advisor	ENVIRON	207-347-4413	6/23	Investigative Organization's Technical Support
Richard Wenning	Project Manager	ENVIRON	510-420-2556	6/20, 6/23	Investigative Organization's Project Coordinator
Tom Vetrano	Project Manager	ENVIRON	973-286-4261	6/20	Investigative Organization's Quality Assurance Coordinator

QAPP Worksheet #10
Problem Definition

PROBLEM DEFINITION

In December 2010, the United States Environmental Protection Agency (USEPA) presented evidence to the Lower Passaic River Cooperating Parties Group (CPG) asserting that there was sufficient evidence supporting a second source of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) to the Lower Passaic River located in the sediment deposit near river mile (RM) 10.9 on the eastern bank of the Passaic River.

PROJECT DESCRIPTION – INVESTIGATION OVERVIEW

This focused sediment investigation strategy is planned as a single field effort with a tiered sample analysis plan and will include the collection of sediment samples from cores at seven (7) locations within the Lower Passaic River Study Area (LPRSA). The cores will be advanced using vibracore methods performed from a boat or barge. Sediment cores will be segmented and sampled at 6-inch intervals. Recovered samples will be shipped to multiple offsite laboratories for analysis of 1,2,4,5,7,8-hexachloro(9H)xanthene (HCX), 17 dioxin/furan congeners, and potentially, Cs-137. The laboratory will be instructed to analyze selected sediment samples upon receipt. Based on the results of the initial sediment sample analyses, additional analyses may be performed on the remaining sediment samples. All sample results will be reported with full data deliverable laboratory packages. All laboratory data generated during the Focused Sediment Investigation Work Plan will undergo full data validation per the procedures listed in Worksheet #36, by an independent data validator.

DATA USE OBJECTIVES

Data generated as part of the focused sediment investigation will be used to further evaluate additional sources of 2,3,7,8-TCDD to the LPRSA.

QAPP Worksheet #11
Project Quality Objectives/Systematic Planning Process Statements

WHO WILL USE THE DATA?

These data will be used by Tierra and its authorized representatives, including Tierra's Legal Defense Team.

WHAT WILL THE DATA BE USED FOR?

These data will be used to identify additional sources of 2,3,7,8-TCDD to RM 10.9, as well as to downstream sections of the LPRSA.

WHAT TYPE OF DATA ARE NEEDED?

The focused sediment investigation will include the collection of sediment samples for laboratory analysis of the following parameters:

- PCDDs/PCDFs using USEPA Method 1613B;
- HCX determination using Extraction and Analysis of HRGC/HRMS Analysis, Vista August 2011
- Radiochemistry for Cs-137 using ALS SOP 739 Rev.10 and 713 Rev.12 (optional)

HOW MUCH DATA ARE NEEDED?

The focused sediment investigation sampling strategy is planned as a single field effort with a tiered sample analysis plan and will include the collection of sediment samples from cores collected at 7 locations within the LPRSA. Cores will be advanced to approximately 4 to 7 feet below the mudline with sediment samples collected at 6-inch intervals. Accordingly, approximately 82 sediment samples (plus quality control samples) will be collected. Analyses performed on sediment samples will be done based upon a tiered hierarchy where an initial set of 61 priority locations will be analyzed for 1,2,4,5,7,8-hexachloro(9H)xanthene and polychlorinated dibenzo-*p*-dioxin/furans (cesium-137 may be analyzed as an option at the project team's discretion). The remaining 21 sample segments will be analyzed for 1,2,4,5,7,8-hexachloro(9H)xanthene and/or polychlorinated dibenzo-*p*-dioxin/furans as determined necessary by the project team.

QAPP Worksheet #11
Project Quality Objectives/Systematic Planning Process Statements (Continued)

HOW GOOD DO DATA NEED TO BE?

Data generated as part of the focused sediment investigation must be adequate to evaluate additional sources of dioxin in the vicinity of RM 10.9 and analytical methods were selected such that detection limits will not limit the usefulness of the data set. Specific sections of the LPRSA targeted for the focused sediment investigation have been prioritized based on 1) 2,3,7,8-TCDD concentrations at depth; 2) presence of stable sediments; 3) identification by Garvey, E., Atmadja, J., Gbondo-Tugbawa, S., McDonald, S. [2011. Dioxin in the Passaic River (NJ): The Case for 2 Dioxin Sources. The Louis Berger Group, Inc. *Battelle Sixth International Conference on the Remediation of Contaminated Sediments Orleans. New Orleans, LA February 10, 2011]* and 4) river morphology.

WHEN WILL DATA BE COLLECTED?

Data are planned to be collected during week 9/15/11 to 9/22/11.

QAPP Worksheet #12-1
Measurement Performance Criteria Table – Rinsate Blanks[a]

Matrix	Rinsate Blanks
Analytical Group[b]	HCX
Concentration Level	Low

Sampling Procedure[c]	Analytical Method/SOP[d]	Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-1	L-1	Accuracy/Bias Contamination	No target compounds ≥PQL	Method Blanks	A
		Accuracy/Bias	HCX recovery (50-150%)	Ongoing Precision and Recovery	A
		Completeness	>90% sample collection,>90% laboratory analysis	Data Completeness Checks	S & A
		Accuracy/Bias	Per L-2	Initial Calibration	A
		Accuracy/Bias	Per L-2	Calibration Verification	A
		Accuracy/Bias	Per L-2	Labeled Internal Standard	A

See the last page of Worksheet #12-1 for a description of footnotes.

QAPP Worksheet #12-1
Measurement Performance Criteria Table – Rinsate Blanks[a] (Continued)

Matrix	Rinsate Blanks
Analytical Group[b]	PCDDs/PCDFs
Concentration Level	Low

Sampling Procedure[c]	Analytical Method/SOP[d]	Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S & A)
SOP-1	L-2	Accuracy/Bias Contamination	No target compounds ≥PQL	Method Blanks	A
		Accuracy/Bias	All target compound concentrations must fall within range provided in Table 6 of L-3	Ongoing Precision and Recovery	A
		Completeness	>90% sample collection, >90% laboratory analysis	Data Completeness Checks	S & A
		Accuracy/Bias	Per L-3	Initial Calibration	A
		Accuracy/Bias	Per L-3	Calibration Verification	A
		Accuracy/Bias	Per L-3	Labeled Compound Spike	A
		Accuracy/Bias	Per L-3	Labeled Internal Standards	A

Notes:

[a] Field and Rinse blanks not required for Cesium-137 (Cs-137).
[b] If information varies within an analytical group, separate by individual analyte.
[c] Reference number from QAPP Worksheet #21.
[d] Reference number from QAPP Worksheet #23.

HCX = 1,2,4,5,7,8-hexachloro(9H)xanthene
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxin s/polychlorinated dibenzofurans
PQL= project quantitation limit
QC = quality control
SOP = Standard Operating Procedure

QAPP Worksheet #12-2
Measurement Performance Criteria Table – Sediment

Matrix	Sediment
Analytical Group[a]	HCX
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators	Measurement Performance Criteria	QA Sample and/or Activity Used to Assess Measurement Performance	QA Sample Assesses Error for Sampling (S), Analytical (A) or Both (S & A)
SOP-3, SOP-4 and SOP-5	L-1	Accuracy/Bias Contamination	No target analytes ≥ PQL	Method Blanks and Rinsate Blanks	S & A
		Accuracy/Bias	HCX recovery (50-150%)	Matrix Spike	A
		Precision	RPD ≤20%	Matrix Spike Duplicate	A

See the last page of Worksheet #12-2 for a description of footnotes

QAPP Worksheet #12-2
Measurement Performance Criteria Table – Sediment (Continued)

Matrix	Sediment
Analytical Group[a]	HCX
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators	Measurement Performance Criteria	QA Sample and/or Activity Used to Assess Measurement Performance	QA Sample Assesses Error for Sampling (S), Analytical (A) or Both (S & A)
SOP-3, SOP-4, and SOP-5	L-1	Accuracy/Bias	HCX recovery (50-150%)	Ongoing Precision and Recovery	A
		Precision-Overall	RPD ≤ 50% when target is detected in both field duplicate samples at ≥ 5x the PQL, or concentrations differ by less than 2x the PQL when detects are < 5x PQL for both field duplicate samples.	Subsample Field Duplicate	S & A
		Completeness	> 90% sample collection, > 90% laboratory analysis	Data Completeness Assessment	S & A
		Accuracy/Bias	Per L-2	Initial Calibration	A
		Accuracy/Bias	Per L-2	Calibration Verification	A
		Accuracy/Bias	Per L-2	Labeled Internal Standards	A

See the last page of Worksheet #12-2 for a description of footnotes

QAPP Worksheet #12-2
Measurement Performance Criteria Table – Sediment (Continued)

Matrix	Sediment
Analytical Group[a]	PCDDs/PCDFs
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators	Measurement Performance Criteria		QA Sample and/or Activity Used to Assess Measurement Performance	QA Sample Assesses Error for Sampling (S), Analytical (A) or Both (S & A)
SOP-3, SOP-4 and SOP-5	L-2	Accuracy/Bias Contamination	No target analytes >_PQL		Method Blanks and Rinsate Blanks	S & A
		Accuracy/Bias	**Compound** All target analytes	**% Recovery** 60-140	Matrix Spike	A
		Precision	**Compound** All target analytes	**RPD** <50%	Matrix Spike Duplicate	A
		Accuracy/Bias	All target analyte concentrations must fall within range provided in Table 6 of L-3		Ongoing Precision and Recovery	A
		Precision-Overall	RPD ≤50% when target is detected in both field duplicate samples at >5X PQL, or concentrations differ by less than 2X the PQL when detects are < 5X PQL for both field duplicate samples		Subsample Field Duplicate	S & A
		Completeness	>90% sample collection, >90% laboratory analysis		Data Completeness Assessment	S & A

See the last page of Worksheet #12-2 for a description of footnotes

QAPP Worksheet #12-2
Measurement Performance Criteria Table – Sediment (Continued)

Matrix	Sediment
Analytical Group[a]	PCDDs/PCDFs
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators	Measurement Performance Criteria	QA Sample and/or Activity Used to Assess Measurement Performance	QA Sample Assesses Error for Sampling (S), Analytical (A) or Both (S & A)
SOP-3, SOP-4 and SOP-5	L-2	Accuracy/Bias	Per L-3	Initial Calibration	A
		Accuracy/Bias	Per L-3	Calibration Verification	A
		Accuracy/Bias	Per L-3	Labeled Compound Spike	A
		Accuracy/Bias	Per L-3	Labeled Internal Standards	A

See the last page of Worksheet #12-2 for a description of footnotes

QAPP Worksheet #12-2
Measurement Performance Criteria Table – Sediment (Continued)

Matrix	Sediment
Analytical Group[a]	Cs-137
Concentration Level	Low

Sampling Procedure[b]	Analytical Method/SOP[c]	Data Quality Indicators	Measurement Performance Criteria	QA Sample and/or Activity Used to Assess Measurement Performance	QA Sample Assesses Error for Sampling (S), Analytical (A) or Both (S & A)
SOP-3, SOP-4 and SOP-5	L-3	Precision-Overall	Activity reported for each of the two field duplicate samples should differ by no more than 2-sigma bands	Subsample Field Duplicate	S & A
		Precision	Activity reported for each of the two duplicate samples should differ by no more than 2-sigma bands	Laboratory Duplicate	A
		Accuracy/Bias	Cs-137 recovery (70-130%)	Laboratory Control Sample	A
		Completeness	>90% sample collection, >90% laboratory analysis	Data Completeness Assessment	S & A

Notes:

[a] If information varies within an analytical group, separate by individual analyte.
[b] Reference number from QAPP Worksheet #21.
[c] Reference number from QAPP Worksheet #23.

Cs-137 = Cesium-137
HCX = 1,2,4,5,7,8-hexachloro(9H)xanthene
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxin s/polychlorinated dibenzofurans
PQL= project quantitation limit
QA = quality assurance
RPD = relative percent difference
SOP = Standard Operating Procedure

QAPP Worksheet #13
Secondary Data Criteria and Limitations

Secondary Data	Data Source (Originating Organization, Report Title, and Date)	Data Generator(s) (Originating Organization, Data Types, Data Generation/Collection Dates)	How Data Will Be Used	Limitations and Data Use
Probing and core data from pre-coring reconnaissance work	USEPA sampling program conducted by MPI, No report (data from USEPA database), 2007 to 2008.	USEPA; Data types include inference on sediment type and thickness (probing) as well as sediment description (cores); December 2007 to June 2008.	Data provides details on recent surficial sediment conditions	Subjective delineation and identification method subject to different interpretations. Comparison of core logs and these data required to verify results.
Analytical data from the LPR high resolution core program	USEPA sampling program conducted by MPI, No report (data from USEPA database), 2005.	USEPA; Data types include sediment dating (Cs-137, Be-7) and contaminant concentrations (PCDD/PCDF, PCBs, PAHs, pesticides, metals). Cores collected September 9, 2005 to October 12, 2005.	Data were used to map horizontal and vertical chemical distribution	Only 5 sediment cores were analyzed for limited and selected chemical parameters. 14 analyzed for Cs-137 over a 10-mile interval. Not all segments from all cores were analyzed. Cores in erosional areas were either not utilized or not fully analyzed. Several cores did not produce recovery required by SOP. Summary narrative provided. Characterization report not produced to document field or analytical activities. Use data with the recognition that laboratory and/or validation qualifiers may impose limitations on specific datasets and/or data points.
Analytical data from grab samples and sediment cores	USEPA EMBM Sampling Program, No report (data from USEPA database), 2007 to 2008.	USEPA; Data types include sediment cores and grab samples analyzed for organic and inorganic contaminants; December 2007 to February 2008.	Data were used to evaluate various organic and inorganic chemicals	Samples collected using vibracoring should be interpreted noting individual core recovery and the uncertainty of vertical placement of the recovered samples. Use data with the recognition that laboratory and/or validation qualifiers may impose limitations on specific datasets and/or data points. Five locations in the vicinity of RM 10.9 silt deposit (EMBM-LR 12, - LR 14, - LR15 and Location 5).

QAPP Worksheet #13
Secondary Data Criteria and Limitations (Continued)

Secondary Data	Data Source (Originating Organization, Report Title, and Date)	Data Generator(s) (Originating Organization, Data Types, Data Generation/Collection Dates)	How Data Will Be Used	Limitations and Data Use
Low Resolution Coring Report	Lower Passaic River Cooperating Parties Group, Low Resolution Coring Characterization Summary Lower Passaic River Study Area RI/FS, February, 2010.	AECOM, Inc.; Data types include 2,3,7,8-TCDD, total TCDD; Cs-137; Pb-210; herbicides, PCBs, PAHs, SVOCs, grain size, and other analytes; July, 2008 to December, 2008.	Data were used to evaluate various organic/inorganic chemicals, radiochemistry, and geotechnical data	Samples collected using vibracoring should be interpreted noting individual core recovery and the uncertainty of vertical placement of the recovered samples. Use data with the recognition that laboratory and/or validation qualifiers may impose limitations on specific datasets and/or data points. Data from only one core in the vicinity of RM 10.9.
Analytical data from grab samples collected for sediment dating	USEPA sampling program conducted by MPI, No report (data from USEPA database), 2005.	USEPA (collected by MPI); Data type includes Be-7; 45 locations, August, 2005.	Data were used to provide insight into potential depositional areas	Characterization report not produced to document field or analytical activities.
Bathymetric surveys	CPG; Bathymetric Survey; 2007; Multibeam Survey, 2010.	CPG; Data types include multibeam and single beam survey performed by GBA (subcontractor to ENSR); August, 2007 to September 2007, and multibeam surveys performed by GBA (subcontractor to AECOM), November, 2008 and June, 2010.	Data were used to characterize existing bathymetry	Single beam coverage limited to RM 0.5 – 8.2 and 14.3 – 16.5. Current only as of the date of survey (i.e., Aug. 2007). Multibeam coverage limited to RM 0 – 14.4 and to the channel area in RM 0 – 0.9. Current only as of the date of the surveys (i.e., Aug. 2007, November 2008 and June 2010). Multibeam coverage limited to RM 0 – 14.4, and to channel area in RM0 – 0.9. Data limited to water depths > -6 feet NGVD.

QAPP Worksheet #14
Summary of Project Tasks

Sampling Tasks:

1. Sediment chemistry sample collection is to be performed by ENVIRON. All field procedures including sampling documentation and decontamination processes are provided in Appendix A.

Analysis Tasks:

1. Vista Analytical will prepare and analyze sediment samples for HCX and PCDDs/PCDFs. Analytical procedures are provided in Appendix B.

2. ALS Environmental may prepare and analyze selected sediment samples for Cs-137 at the project team's discretion. Analytical procedures are provided in Appendix B.

Quality Control Tasks:

1. All field and laboratory procedures will be carried out per the SOPs and methodologies provided in Appendices A and B, respectively. In addition, field and laboratory quality control samples will be processed as indicated in Worksheets #28-1 and 28-2. Project quality objectives and measurement performance criteria will be monitored throughout project implementation and at the conclusion of field and analytical activities. All data produced will undergo data verification/validation steps specified in Worksheets #34, 35 and 36. These data evaluation steps will be performed by an organization independent from those generating the data.

Secondary Data:

1. See Worksheet #13.

Data Management Tasks:

1. Hardcopy data and records are placed in the project file. Refer to Section 3 of Worksheet #27.

2. Analytical data will be placed in a database after verification/validation.

QAPP Worksheet #15-1
Reference Limits and Evaluation – Water

Matrix: Rinsate Blank
Analytical Group: HCX
Concentration Level: Low
Analytical Method/SOP Reference: L-1

Analyte	CAS Number	Project Quantitation Limit pg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
			MDLs pg/L	Method QLs pg/L	MDLs pg/L	QLs pg/L
HCX	38178-99-3	50	N/A	N/A	34.59	50

See the last page of Worksheet #15-1 for footnotes.

QAPP Worksheet #15-1
Reference Limits and Evaluation – Water

Matrix: Rinsate Blank
Analytical Group: PCDDs/PCDFs
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Project Quantitation Limit pg/L	Analytical Method[a]		Achievable Laboratory Limits[b]	
			MDLs pg/L	Method QLs pg/L	MDLs pg/L	QLs pg/L
2,3,7,8-TCDD	1746-01-6	5	Not provided in method	10	.93	5
1,2,3,7,8-PeCDD	40321-76-4	25	Not provided in method	50	1.77	25
1,2,3,6,7,8-HxCDD	57653-85-7	25	Not provided in method	50	1.13	25
1,2,3,4,7,8-HxCDD	39227-28-6	25	Not provided in method	50	1.05	25
1,2,3,7,8,9-HxCDD	19408-74-3	25	Not provided in method	50	2.22	25
1,2,3,4,6,7,8-HpCDD	35822-46-9	25	Not provided in method	50	1.93	25
OCDD	3268-87-9	50	Not provided in method	100	1.65	50
2,3,7,8-TCDF	51207-31-9	5	Not provided in method	10	.26	5
1,2,3,7,8-PeCDF	57117-41-6	25	Not provided in method	50	1.92	25
2,3,4,7,8-PeCDF	57117-31-4	25	Not provided in method	50	0.97	25
1,2,3,6,7,8-HxCDF	57117-44-9	25	Not provided in method	50	1.15	25
1,2,3,7,8,9-HxCDF	72918-21-9	25	Not provided in method	50	1.18	25
1,2,3,4,7,8-HxCDF	70648-26-9	25	Not provided in method	50	1.22	25
2,3,4,6,7,8-HxCDF	60851-34-5	25	Not provided in method	50	1.41	25
1,2,3,4,6,7,8-HpCDF	67562-39-4	25	Not provided in method	50	0.85	25
1,2,3,4,7,8,9-HpCDF	55673-89-7	25	Not provided in method	50	2.24	25
OCDF	39001-02-0	50	Not provided in method	100	1.34	50

See the last page of Worksheet #15-1 for footnotes.

QAPP Worksheet #15-1
Reference Limits and Evaluation – Water (Continued)

Notes:

[a] – Analytical MDLs and QLs are those documented in the validated methods.
[b] – Achievable Laboratory Limits are limits that the laboratory can achieve when performing a specific analytical method.

HCX = 1,2,4,7,8-hexachloro(9H)xanthene
MDL = method detection limit
N/A = not applicable
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
pg/L = picograms per liter
PQL = project quantitation limit
QL = quantitation limit
TBD = to be determined

QAPP Worksheet #15-2
Reference Limits and Evaluation – Sediment

Matrix: Sediment
Analytical Group: HCX
Concentration Level: Low
Analytical Method/SOP Reference: L-1

Analyte	CAS Number	Project Quantitation Limit pg/g	Analytical Method[a]		Achievable Laboratory Limits[b]	
			MDLs pg/g	Method QLs pg/g	MDLs pg/g	QLs pg/g
HCX	38178-99-3	20	N/A	N/A	11.40	20

See the last page of Worksheet #15-2 for footnotes.

QAPP Worksheet #15-2
Reference Limits and Evaluation – Sediment

Matrix: Sediment
Analytical Group: PCDDs/PCDFs
Concentration Level: Low
Analytical Method/SOP Reference: L-2

Analyte	CAS Number	Project Quantitation Limit pg/g	Analytical Method[a]		Achievable Laboratory Limits[b]	
			MDLs pg/g	Method QLs pg/g	MDLs pg/g	QLs pg/g
2,3,7,8-TCDD	1746-01-6	0.5	Not provided in method	1	0.05	0.5
1,2,3,7,8-PeCDD	40321-76-4	2.5	Not provided in method	5	0.13	2.5
1,2,3,6,7,8-HxCDD	57653-85-7	2.5	Not provided in method	5	0.14	2.5
1,2,3,4,7,8-HxCDD	39227-28-6	2.5	Not provided in method	5	0.10	2.5
1,2,3,7,8,9-HxCDD	19408-74-3	2.5	Not provided in method	5	0.24	2.5
1,2,3,4,6,7,8-HpCDD	35822-46-9	2.5	Not provided in method	5	0.16	2.5
OCDD	3268-87-9	5.0	Not provided in method	10	0.99	5.0
2,3,7,8-TCDF	51207-31-9	0.5	Not provided in method	1	0.07	0.5
1,2,3,7,8-PeCDF	57117-41-6	2.5	Not provided in method	5	0.22	2.5
2,3,4,7,8-PeCDF	57117-31-4	2.5	Not provided in method	5	0.28	2.5
1,2,3,6,7,8-HxCDF	57117-44-9	2.5	Not provided in method	5	0.35	2.5
1,2,3,7,8,9-HxCDF	72918-21-9	2.5	Not provided in method	5	0.25	2.5
1,2,3,4,7,8-HxCDF	70648-26-9	2.5	Not provided in method	5	0.24	2.5
2,3,4,6,7,8-HxCDF	60851-34-5	2.5	Not provided in method	5	0.30	2.5
1,2,3,4,6,7,8-HpCDF	67562-39-4	2.5	Not provided in method	5	0.18	2.5
1,2,3,4,7,8,9-HpCDF	55673-89-7	2.5	Not provided in method	5	0.30	2.5
OCDF	39001-02-0	5.0	Not provided in method	10	0.72	5.0

See the last page of Worksheet #15-2 for footnotes.

QAPP Worksheet #15-2
Reference Limits and Evaluation – Sediment

Matrix: Sediment
Analytical Group: Cs-137
Concentration Level: Low
Analytical Method/SOP Reference: L-3

Analyte	CAS Number	Project Quantitation Limit pCi/g	Analytical Method[a]		Achievable Laboratory Limits[b]	
			MDLs pCi/g	Method QLs pCi/g	MDLs pCi/g	QLs pCi/g
Cs-137	10045-97-3	0.1pCi/g[c]	N/A	N/A	N/A	N/A

See the last page of Worksheet #15-2 for footnotes.

QAPP Worksheet #15-2
Reference Limits and Evaluation (Continued)

Notes:

[a] Analytical MDLs and QLs are those documented in the validated methods.
[b] Achievable Laboratory Limits are limits that the laboratory can achieve when performing a specific analytical method. These values will be obtained from the laboratory selected to perform given task on a property specific basis and will be included in the appropriate SAP.
[c] Project Quantitation Limit Represents the Minimum Detectable Concentration as defined below:

Project reporting limit goals for radiochemistry parameters are sample specific values expressed as minimum detectable concentration (MDC). The MDC values achieved for radiochemistry target analyte will be less than or equal to the PQLs listed in table 5-21.

Use the equation below to perform the MDC calculations:

$$MDC = \frac{4.65\sqrt{BC} + 2.71}{KT}$$

Where:

BC = the total counts in the background for the sample
T = the sample counting time
K = the constant representing sample volume, detector efficiency, chemical recovery, decay factor, unit corrections, and any other applicable conversion factors.

Although MDC is used as the reporting limit goal for radiochemistry analyses, all radiochemistry sample readings will be reported as measured. A separate calculation will be performed by the laboratory to determine a sample-specific critical value (CV) which is also reported along with the measured activity reading.

Use the equation below to perform the CV calculations:

$$CV = \frac{2.33\sqrt{BC}}{KT}$$

Where:

BC = the total counts in the background for the sample
T = the sample counting time
K = the constant representing sample volume, detector efficiency, chemical recovery, decay factor, unit corrections, and any other applicable conversion factors.

QAPP Worksheet #15-2
Reference Limits and Evaluation (Continued)

Notes:

CAS = Chemical Abstracts Service
Cs = Cesium-137
HCX = 1,2,4,5,7,8-hexachloro(9H)xanthene
MDL = method detection limit
N/A = not applicable
PCDDs/PCDFs= polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
pCi/g = picocurie per gram
pg/g = picogram per gram
PQL = project quantitation limit
QL = quantitation limit
TBD = to be determined

QAPP Worksheet #16
Project Schedule/Timeline

Activities	Organization	Dates (MM/DD/YY)		Deliverable	Deliverable Due Date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
Compilation and Interpretation of Sediment Data in the Vicinity of RM 10.9	ENVIRON	5/16/11	7/29/11	Sediment Data Interpretation Report	7/29/11
Preparation of FSIWP/QAPP	ENVIRON, EDS	5/16/11	8/12/11	FSIWP/QAPP	8/12/11
Revisions to FSIWP/QAPP	ENVIRON, EDS	8/12/11	8/29/11	FSIWP/QAPP	8/29/11
Field Readiness Review	ENVIRON	9/12/11	9/15/11	Participant Sign-off Sheet	9/15/11
Laboratory Readiness Review	EDS	9/12/11	9/15/11	Participant Sign-off Sheet	9/15/11
Sediment Collection and Processing	ENVIRON, OSI	9/15/11	9/22/11	--	9/22/11
Sediment Analysis	Vista, ALS Environmental	9/19/11	11/2/11	Laboratory Data Packages	11/2/11
Data Validation	EDS	11/2/11	12/12/11	Data Validation Reports	12/12/11
Data Usability Assessment	EDS	12/12/11	1/18/12	Data Quality Assessment Report	1/18/11
Data Management	ENVIRON	10/3/11	1/2/12	Updated Project Database	1/2/12
Data Review / Assessment and Preparation of Report Deliverable	ENVIRON	10/3/11	2/2/12	Field Report and HCX Characterization Study	2/12/112

QAPP Worksheet #17
Sampling Design and Rationale

In general, judgmental sampling design was utilized in developing the FSIWP. This approach relies on existing information and professional judgment, without any type of randomization. Sediment sampling locations were selected based on a number of considerations, including: 2,3,7,8-TCDD analytical results obtained during prior sediment sampling activities within the LPRSA, river morphology, the presence of stable sediments, and, to some extent, accessibility (e.g., available water depth at high tide).

The focused sediment investigation will include the collection of sediment samples from cores advanced at seven (7) locations within the LPRSA. Cores will be advanced to approximately 4 to 7 feet below the mudline with sediment samples collected at 6-inch intervals. Accordingly, approximately 82 sediment samples (plus quality control samples) will be collected. Selected sediment sample segments will be analyzed for 1,2,4,5,7,8-hexachloro(9H)xanthene (HCX) and PCDDs/PCDFs and potentially Cs-137 as an optional determination as part of the focused sediment investigation. The project area and proposed sampling locations are depicted on Figures 1 through 4. Specific rationale for each proposed sediment sampling location is provided below.

A1, A2 and A3 – The proposed boring locations are located on a mudflat/point bar at RM 10.9 approximately 0.2 to 0.3 miles downstream of the confluence of the Third River and Passaic River. Prior sediment sampling activities completed at RM 10.9 identified 2,3,7,8-TCDD concentrations ranging over 30,000 parts per trillion (ppt).

B1 and B2 – These proposed boring locations are positioned near the western shore of the Passaic River at RM 11.5. Prior sediment sampling activities completed at RM 11.5 identified 2,3,7,8-TCDD concentrations ranging up to 6,200 ppt.

C1 and C2 – These proposed boring locations are positioned near the western shore of the Passaic River at RM 7.8. Prior sediment sampling activities completed at RM 7.8 identified 2,3,7,8-TCDD concentrations ranging up to 6,000 ppt.

QAPP Worksheet #18
Sampling Locations and Methods / SOP Requirements

Matrix: Sediment
Concentration Level: Low

Sampling Location	Estimated Core Length (feet)	Sample ID	Sample Depth Interval (inches)	Analytical Group			Number of Samples	Sampling SOP Reference	Rationale for Sampling Location
				PCDDs/PCDFs	HCX	Cs-137			
A1	7	A01-SD1-000-006	0 - 6	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A1	7	A01- SD1-006-012	6 - 12	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A1	7	A01- SD1-012-018	12 - 18	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A1	7	A01- SD1-018-024	18 - 24	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A1	7	A01- SD1-024-030	24 - 30	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A1	7	A01- SD1-030-036	30 - 36	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A1	7	A01-SD1-036-042	36 - 42	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A1	7	A01-SD1-042-048	42 - 48	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A1	7	A01-SD1-048-054	48 - 54	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A1	7	A01-SD1-054-060	54 - 60	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A1	7	A01-SD1-060-066	60 - 66	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A1	7	A01-SD1-066-072	66 - 72	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A1	7	A01-SD1-072-078	72 - 78	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A1	7	A01-SD1-078-084	78 - 84	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17

See last page of Worksheet #18 for a description of notes.

QAPP Worksheet #18
Sampling Locations and Methods / SOP Requirements (Continued)

Matrix: Sediment
Concentration Level: Low

Sampling Location	Estimated Core Length (feet)	Sample ID	Sample Depth Interval (inches)	Analytical Group			Number of Samples	Sampling SOP Reference	Rationale for Sampling Location
				PCDDs/PCDFs	HCX	Cs-137			
A2	6	A02-SD1-000-006	0 - 6	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A2	6	A02-SD1-006-012	6 - 12	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A2	6	A02-SD1-012-018	12 - 18	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A2	6	A02-SD1-018-024	18 - 24	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A2	6	A02-SD1-024-030	24 - 30	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A2	6	A02-SD1-030-036	30 - 36	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A2	6	A02-SD1-036-042	36 - 42	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A2	6	A02-SD1-042-048	42 - 48	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A2	6	A02-SD1-048-054	48 - 54	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A2	6	A02-SD1-054-060	54 - 60	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A2	6	A02-SD1-060-066	60 - 66	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A2	6	A02-SD1-066-072	66 - 72	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17

See last page of Worksheet #18 for a description of notes.

QAPP Worksheet #18
Sampling Locations and Methods / SOP Requirements (Continued)

Matrix: Sediment
Concentration Level: Low

Sampling Location	Estimated Core Length (feet)	Sample ID	Sample Depth Interval (inches)	Analytical Group			Number of Samples	Sampling SOP Reference	Rationale for Sampling Location
				PCDDs/PCDFs	HCX	Cs-137			
A3	7	A03-SD1-000-006	0 - 6	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A3	7	A03-SD1-006-012	6 - 12	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A3	7	A03-SD1-012-018	12 - 18	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A3	7	A03-SD1-018-024	18 - 24	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A3	7	A03-SD1-024-030	24 - 30	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A3	7	A03-SD1-030-036	30 - 36	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A3	7	A03-SD1-036-042	36 - 42	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A3	7	A03-SD1-042-048	42 - 48	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A3	7	A03-SD1-048-054	48 - 54	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A3	7	A03-SD1-054-060	54 - 60	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A3	7	A03-SD1-060-066	60 - 66	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A3	7	A03-SD1-066-072	66 - 72	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A3	7	A03-SD1-072-078	72 - 78	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
A3	7	A03-SD1-078-084	78 - 84	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17

See last page of Worksheet #18 for a description of notes.

QAPP Worksheet #18
Sampling Locations and Methods / SOP Requirements (Continued)

Matrix: Sediment
Concentration Level: Low

Sampling Location	Estimated Core Length (feet)	Sample ID	Sample Depth Interval (inches)	Analytical Group			Number of Samples	Sampling SOP Reference	Rationale for Sampling Location
				PCDDs/PCDFs	HCX	Cs-137			
B1	4	B01-SD1-000-006	0 - 6	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B1	4	B01-SD1-006-012	6 - 12	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B1	4	B01-SD1-012-018	12 - 18	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B1	4	B01-SD1-018-024	18 - 24	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B1	4	B01-SD1-024-030	24 - 30	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B1	4	B01-SD1-030-036	30 - 36	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B1	4	B01-SD1-036-042	36 - 42	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B1	4	B01-SD1-042-048	42 - 48	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B2	6	B02-SD1-000-006	0 - 6	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B2	6	B02-SD1-006-012	6 - 12	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B2	6	B02-SD1-012-018	12 - 18	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B2	6	B02-SD1-018-024	18 - 24	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B2	6	B02-SD1-024-030	24 - 30	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B2	6	B02-SD1-030-036	30 - 36	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B2	6	B02-SD1-036-042	36 - 42	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B2	6	B02-SD1-042-048	42 - 48	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17

See last page of Worksheet #18 for a description of notes.

QAPP Worksheet #18
Sampling Locations and Methods / SOP Requirements (Continued)

Matrix: Sediment
Concentration Level: Low

Sampling Location	Estimated Core Length (feet)	Sample ID	Sample Depth Interval (inches)	Analytical Group			Number of Samples	Sampling SOP Reference	Rationale for Sampling Location
				PCDDs/PCDFs	HCX	Cs-137			
B2	6	B02-SD1-048-054	48 - 54	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B2	6	B02-SD1-054-060	54 - 60	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B2	6	B02-SD1-060-066	60 - 66	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
B2	6	B02-SD1-066-072	66 - 72	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C1	5	C01SD1-000-006	0 - 6	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C1	5	C01-SD1-006-012	6 - 12	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C1	5	C01-SD1-012-018	12 - 18	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C1	5	C01-SD1-018-024	18 - 24	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C1	5	C01-SD1-024-030	24 - 30	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C1	5	C01-SD1-030-036	30 - 36	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C1	5	C01-SD1-036-042	36 - 42	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C1	5	C01-SD1-042-048	42 - 48	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C1	5	C01-SD1-048-054	48 - 54	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C1	5	C01-SD1-054-060	54 - 60	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17

See last page of Worksheet #18 for a description of notes.

QAPP Worksheet #18
Sampling Locations and Methods / SOP Requirements (Continued)

Matrix: Sediment
Concentration Level: Low

Sampling Location	Estimated Core Length (feet)	Sample ID	Sample Depth Interval (inches)	Analytical Group			Number of Samples	Sampling SOP Reference	Rationale for Sampling Location
				PCDDs/PCDFs	HCX	Cs-137			
C2	6	C02-SD1-000-006	0 - 6	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C2	6	C02-SD1-006-012	6 - 12	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C2	6	C02-SD1-012-018	12 - 18	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C2	6	C02-SD1-018-024	18 - 24	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C2	6	C02-SD1-024-030	24 - 30	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C2	6	C02-SD1-030-036	30 - 36	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C2	6	C02-SD1-036-042	36 - 42	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C2	6	C02-SD1-042-048	42 - 48	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C2	6	C02-SD1-048-054	48 - 54	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C2	6	C02-SD1-054-060	54 - 60	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C2	6	C02-SD1-060-066	60 - 66	A	A	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17
C2	6	C02-SD1-066-072	66 - 72	H	H	H	1	SOP-3, SOP-4, SOP-5	See Worksheet #17

Notes:

A = analyze
H = will be held and analyzed at the project team's discretion

QAPP Worksheet #19
Analytical SOP Requirements - Rinsate Blanks

Matrix	Analytical Group	Concentration Level	Analytical SOP Reference[a]	Sample Volume[b]	Containers (number, size and type)[c]	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)[d]
Rinsate Blanks[e]	HCX	Low	L-1	1 L	1 L, G	Cool 4°C	14 days to extraction , 40 days until analysis
	PCDDs/PCDFs	Low	L-2	1 L	1 L, G	Cool 4°C	30 days to extraction , 45 days until analysis

Notes:

[a] Analytical methods are as specified in Worksheet #23-1.
[b] These are minimum sample volume requirements for a single sample analysis. Extra volume will be needed in order to provide contingency volume for reanalysis or breakage.
[c] Samples for analyses having identical container and preservation requirements may be combined in the same container. Similarly, smaller- or larger-sized sample containers than those recommended here may be used as long as the quality, container material, and preservative specifications are met, and the containers or container used will hold sufficient mass/volume to meet the minimum requirements specified.
[d] Holding time is calculated from the date and time of sample collection, to the date and time of sample analysis (or extraction as noted). Maximum holding times listed are based upon those stipulated in corresponding data validation guidance located in Appendix C of this document.
[e] Rinse Blanks are not required for Cs-137 analysis.

°C = degrees Celsius
Cs-137 = Cesium-137
G = amber glass
g = grams
HCX = 1,2,4,5,7,8-hexachloro(9H)xanthene
L= liter
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
SOP = standard operating procedure

QAPP Worksheet #19
Analytical SOP Requirements - Sediment

Matrix	Analytical Group	Concentration Level	Analytical SOP Reference[a]	Sample Mass[b]	Containers (number, size and type)[c]	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)[d]
Sediment	HCX	Low	L-1	50 g	8.8 oz., G[e]	Cool 4°C	14 days to extraction, 40 days until analysis
	PCDDs/PCDFs	Low	L-2	50 g	8.8 oz., G[e]	Cool 4°C	30 days to extraction , 45 days until analysis
	Cs-137	Low	L-3	300 g	8.8 oz., G[e]	N/A	6 months

Notes:

[a] Analytical methods are as specified in Worksheet #23-1.
[b] These are minimum sample mass requirements for a single sample analysis. Extra mass will be needed in order to fulfill quality control sample requirements, such as matrix spike/matrix spike duplicate and/or to provide contingency volume for analysis or breakage.
[c] Samples for analyses having identical container and preservation requirements may be combined in the same container. Similarly, smaller- or larger-sized sample containers than those recommended here may be used as long as the quality, container material, and preservative specifications are met, and the containers or container used will hold sufficient mass/volume to meet the minimum requirements specified.
[d] Holding time is calculated from the date and time of sample collection, to the date and time of sample analysis (or extraction as noted). Maximum holding times listed are based upon those stipulated in corresponding data validation guidance located in Appendix C of this document.
[e] Short, wide-mouth jars with Teflon®-lined lids.

°C = degrees Celsius
Cs-137 = Cesium-137
G = amber glass
HCX = 1,2,4,5,7,8-hexachloro(9H)xanthene
N/A = not applicable
oz. = ounce
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
SOP = standard operating procedure

QAPP Worksheet #20
Sediment Field Quality Control Sample Summary

Concentration Level: Low

Matrix	Analytical Group	Analytical and Preparation Method/SOP Reference[a]	Number of Samples Collected for analysis	Number of Field Duplicate Pairs[b]	Number of MS[c]	Number of MSD or Duplicates[c]	Number of Rinsate Blanks[d]	Number of Samples Collected to be Held for Potential Analysis[e]	Total Number of Samples to Lab[f]
Sediment	HCX	L-1	61	4	4	4	7	22	87
Sediment	PCDDs/PCDFs	L-2	61	4	4	4	7	22	87
Sediment	Cs-137	L-3	N/A	N/A	N/A	N/A	N/A	87	87

Notes:

[a] Referenced from the Analytical SOP References Table (Worksheet #23).
[b] Field duplicate samples will be collected at a frequency of 1 per 20 field samples per matrix, per analytical method, per sample delivery group (SDG).
[c] MS/MSD samples will be collected at a rate of 1 (MS) and 1 (MSD) per up to 20 samples or per SDG (whichever is more frequent) for all constituents except Cs-137, which will have one laboratory duplicate per up to 20 samples collected or per SDG (whichever is more frequent).
[d] Rinsate blanks will be collected at a frequency of one per decontamination event (not to exceed 1 per day) and one pre-project core liner lot check. The number of rinsate blanks listed assumes 6 days of core processing.
[e] Number of samples collected to be held for potential analysis at project team's discretion includes field duplicate samples.
[f] Total number of samples to the lab does not include rinsate blanks.

Cs-137 = Cesium-137
HCX = 1,2,4,5,7,8-hexachloro(9H)xanthene
MS = matrix spike
MSD = matrix spike duplicate
N/A = not applicable
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
SOP = Standard Operating Procedure

QAPP Worksheet #21
Project Sampling SOP References

Reference Number	Title, Revision Date and/or Number	Originating Organization	Modified for Project Work? (Y/N)	Comments
SOP 1	Decontamination	ENVIRON	N	Describes procedures for decontaminating sampling equipment and collecting a rinsate blank.
SOP 2	Positioning	ENVIRON	N	Describes proper positioning of vessel for coring operations using DGPS.
SOP 3	Sediment Collection Using Hand Coring Device	ENVIRON	N	Describes how to collect sediment via manual coring methods; includes procedure to determine acceptable core penetration and core recovery.
SOP 4	Sediment Collection Using Vibracoring Device	ENVIRON	N	Describes how to collect sediment using a vibracore; includes procedure to determine acceptable core penetration and core recovery.
SOP 5	Core Processing	ENVIRON	N	Describes core processing for high and non-high water content sediments; includes calculations for determining bulk density of core.
SOP 6	Management and Disposal of Residuals	ENVIRON	N	Describes procedures for properly disposing of solid, liquid, and chemical wastes, including handling and tracking.
SOP 7	Field Documentation	ENVIRON	N	Describes field documentation procedures; contains daily activity log, core collection form, individual core collection form, core lithology/description form, and sample processing form.
SOP 8	Containers, Preservation, Handling and Tracking of Samples for Analysis	ENVIRON	N	Describes sample handling procedures including preservation of rinsate blanks for various analyses, sample packaging, and sample tracking.
SOP S1	Air Monitoring – Photoionization Detector (PID)	ENVIRON	N	Defines protocols for field operations requiring the use of a PID to monitor vapor concentrations during the implementation of field operations.

QAPP Worksheet #22
Field Equipment Calibration, Maintenance, Testing, and Inspection

Field Equipment	Calibration Activity	Maintenance Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	SOP Reference
Photoionization Detector (PID)	Two-point field calibration using zero and standard reference gas.	Replace / charge batteries as needed. Replace lamp.	Check for damage. Check batteries / power source.	Daily prior to use.	Calibration limits per equipment manufacturer's specification.	If limits are not met, re-calibrate and test acceptance criteria. Replace equipment if calibration is unacceptable.	SOP-S1, SOP-5
Hydrogen Sulfide Meter	Two-point field calibration using zero and standard reference gas.	Replace / charge batteries as needed. Replace sensor, as necessary.	Check batteries / power source. Check expiration date installed on sensor. Check for damage.	Prior to beginning project and every six months thereafter.	Calibration limits per equipment manufacturer's specification.	If limits are not met, re-calibrate and test acceptance criteria. Replace equipment if calibration is unacceptable.	SOP-5
Mercury Vapor Meter	Zero calibration Multi-point NIST traceable permeation tubes	Replace / charge batteries as needed. Replace sensor, as necessary.	Check batteries / power source. Check for damage.	Zero calibration daily prior to use Factory calibration every 12 months	Calibration limits per equipment manufacturer's specification.	If limits are not met, re-calibrate and test acceptance criteria. Replace equipment if calibration is unacceptable.	SOP-5

QAPP Worksheet #22
Field Equipment Calibration, Maintenance, Testing, and Inspection (Continued)

Field Equipment	Calibration Activity	Maintenance Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	SOP Reference
Fathometer	Multi-point field calibration using reference bar.	Replace paper and ink (if applicable). Reset time / date clock as necessary. Replace batteries (as needed).	Check paper and ink supply. Check batteries / power source. Check accuracy of time / date clock.	Twice daily at the beginning and end of the day.	Calibration limits per equipment manufacturer's specification.	If limits are not met, re-calibrate and test acceptance criteria. Replace equipment if calibration is unacceptable.	SOP-3, SOP-4
Differential Global Positioning System (DGPS)	Navigation checks	Replace batteries (as needed).	Check batteries / power source. Inspect for deterioration	Twice daily.	Horizontal accuracy compared to shore-based markers.	If > +/- one meter, verify system performance and evaluate potential antenna and/or antenna cable failure	SOP-2, SOP-3, SOP-4
Survey Equipment	Per manufacturer's instructions to reset control point.	Replace batteries (as needed). Seal cracks and clean build up as necessary.	Inspect for deterioration, buildup, cracks.	Prior to beginning project and twice daily at the beginning and end of the day.	Calibration limits per equipment manufacturer's specification.	If limits are not met, re-calibrate and test acceptance criteria. Replace equipment if calibration is unacceptable.	SOP-2, SOP-3, SOP-4

QAPP Worksheet #22
Field Equipment Calibration, Maintenance, Testing, and Inspection (Continued)

Field Equipment	Calibration Activity	Maintenance Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	SOP Reference
Vibracore	N/A	Fill associated generator with gasoline (if applicable).	Inspect for deterioration, cracks.	N/A	N/A	N/A	SOP-4
Portable and Bench Scale	Two-point calibration using zero and calibration weight.	Replace batteries (as needed).	Check for damage. Check batteries / power source.	Daily, prior to use.	Calibration limits per equipment manufacturer's specifications.	If limits are not met, re-calibrate and test acceptance criteria. Replace equipment if calibration is unacceptable.	SOP-5
Camera	N/A	Replace batteries (as needed).	Check for damage. Check batteries / power source.	N/A	N/A	N/A	SOP-3, SOP-4, SOP-5, SOP-7
Hand-held Oscillating Saw	N/A	Replace blades (as needed).	Check for damage. Check batteries / power source.	N/A	N/A	N/A	SOP-3, SOP-4
Drill	N/A	Replace drill bits (as needed).	Check for damage. Check batteries / power source.	N/A	N/A	N/A	SOP-3, SOP-4

QAPP Worksheet #23
Analytical Method/SOP Reference

Reference Number	Analytical Method/SOP	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
L-1	Extraction and Analysis of Hexachloroxanthene by HRGC/HRMS, Vista 2011	Definitive	HCX	HRGC/HRMS	Vista Analytical Laboratory	N
L-2	USEPA 1613B	Definitive	PCDDs/PCDFs	HRGC/HRMS	Vista Analytical Laboratory	N
L-3	ALS SOP 739 Rev.10 and 713 Rev.12	Definitive	Cesium-137	Gamma Detection	ALS Environmental	N

Notes:

Cs-137 = Cesium-137
HCX = 1,2,4,5,7,8-hexachlor(9H)xanthenes
HRGC/HRMS = high resolution gas chromatography/high resolution mass spectrometry
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
SOP = Standard Operating Procedure
USEPA = United States Environmental Protection Agency

QAPP Worksheet #24
Analytical Instrument Calibration

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	Person Responsible for Corrective Action	SOP Reference[a]
HRGC/HRMS	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	Acceptance criteria for all laboratory instrument calibrations are provided in Appendix B.	Project samples may not be analyzed until all calibration acceptance criteria are met.	Laboratory Analyst	L-1, L-2
Germanium Gamma Spectrometer	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	All laboratory instruments and equipment must be calibrated according to the schedule and procedures specified in the analytical method. Analytical methods are provided in Appendix B.	Acceptance criteria for all laboratory instrument calibrations are provided in Appendix B.	Project samples may not be analyzed until all calibration acceptance criteria are met.	Laboratory Analyst	L-3

Notes:

[a] From the Analytical SOP Reference Table (Worksheet #23)

HRGC/HRMS = high resolution gas chromatograph/high resolution mass spectrometer

QAPP Worksheet #25
Analytical Instrument and Equipment Maintenance, Testing and Inspection

All analytical instruments and equipment must be inspected, maintained, and tested. Procedures for inspection, maintenance, and testing of laboratory instruments and equipment are provided in the laboratory's quality assurance (QA) manuals and associated laboratory Standard Operating Procedures (SOPs).

Documentation of inspections, maintenance, and testing of laboratory instruments and equipment will include details of observed problems, corrective measures, routine maintenance, and instrument repair, including information regarding the repair and the individual who performed the repair.

At a minimum, major instruments will be backed up by comparable (if not equivalent) instrument systems to avoid unscheduled downtime. An inventory of spare parts will also be available to minimize equipment/instrument downtime.

QAPP Worksheet #26
Sampling Handling System

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
Sample Collection (Personnel/Organization): Field Personnel, ENVIRON
Sample Packaging (Personnel/Organization): Field Personnel, ENVIRON
Coordination of Shipment (Personnel/Organization): Field Personnel, ENVIRON
Type of Shipment/Carrier: Field/Laboratory Courier or Federal Express
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (Personnel/Organization): Martha Maier/Vista Analytical Laboratory, Julie Ellingson/ALS Environmental
Sample Custody and Storage (Personnel/Organization): Martha Maier/Vista Analytical Laboratory, Julie Ellingson/ALS Environmental
Sample Preparation (Personnel/Organization): Martha Maier/Vista Analytical Laboratory, Julie Ellingson/ALS Environmental
Sample Determinative Analysis (Personnel/Organization): Martha Maier/Vista Laboratory, Julie Ellingson/ALS Environmental
SAMPLE ARCHIVING
Field Sample Storage (From sample collection): 6 months
Sample Extract/Digestate Storage (From extraction/digestion): 6 months (Samples are to be stored under conditions appropriate for a given analytical group. These conditions are described in Worksheets #19.)
SAMPLE DISPOSAL
Personnel/Organization: Martha Maier/Vista Analytical Laboratory 6 months, Julie Ellingson/ALS Environmental
Samples and/or sample residual material, including jars and containers, will be returned to the Diamond Alkali Superfund Site by the laboratories, but only after the sample archival period expires. No less than 30 days prior to shipment, the laboratory will contact Tierra, in writing, to request final instructions on return shipment of samples and/or sample residual material, including jars and containers, to the Diamond Alkali Superfund Site. Under no circumstances will the laboratories dispose of samples and/or sample residual material, including jars and containers, without the express, written direction of Tierra Solutions, Inc. or their representatives. Residual material will later be containerized at the Diamond Alkali Superfund Site.

QAPP Worksheet #27
Sample Custody Requirements

Sample Custody Procedures

Sample custody, or chain of custody (COC), protocols are in three parts 1) sample collection, 2) laboratory, and 3) final documentary files.

Field sample custody procedures will be implemented to ensure that samples are not tampered with from the time of sample collection through time of transport to the analytical laboratory. Custody of the samples by a given person is defined by: 1) physical possession of the samples (i.e., carrying or holding the samples), 2) having the samples within clear view after having possession, or 3) having physical possession and leaving them in a secure location so that they cannot be tampered with. In addition, when samples are secured in a restricted area accessible only to authorized personnel, they will be deemed to be in the custody of such authorized personnel.

Field custody documentation includes both field log books and field COC forms. Samples will be accompanied by a properly completed COC form. The sample identifiers will be listed on the COC form. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the COC form. This record documents transfer of custody of samples from the sampler to another person, to the laboratory, or to and from a secure storage area. The proper procedures for using a COC form are provided in standard operating procedure (SOP), Appendix A.

1) Sample Collection Custody Procedures

Field Chain of Custody Procedures

The sample packaging and shipment procedures summarized below are designed to confirm that the samples will arrive at the laboratory with the chain of custody intact. The protocols for specific sample numbering and other sample designations are also included.

Field Procedures

The field sampler will be personally responsible for the care and custody of the samples until the samples are transferred. As few people as possible will handle the samples.

Sample containers will be tagged or labeled with unique sample identification numbers (described below), as well as time and date of sample collection. Sample tags or labels will be completed for each sample using pre-printed labels or using permanent, waterproof ink either prior to or immediately after sample collection.

QAPP Worksheet #27
Sample Custody Requirements (Continued)

Sample Identification Code

Appropriate sample containers containing preservatives, if necessary, will be provided by the analytical laboratories. Field personnel will be responsible for confirming the correct number and type of containers for the day's planned field effort and properly labeling containers.

A non-removable (even when wet) label will be affixed to each sample container. Labels will be marked with waterproof indelible ink. The following information will be contained on each label:

- Project and site name
- Sample identifier
- Company (ENVIRON)
- Sample date and time
- Sampler's initials
- Analysis(es) required

Each sample will be assigned a unique alpha-numeric identification that captures the sample location, core, matrix, and sample depth interval. The identification will use the following procedures:

- Three digit sample location designation (e.g., A01);
- Three digit designation to specify primary or secondary core number (i.e., SD1 and SD2, respectively);
- Three digits to indicate the depth to the top of the sample interval in inches;
- Three digits to indicate the depth to the bottom of the sample interval in inches.

For example, the sediment sample collected from 6 to 12 inches below the mudline at the sample location A2 primary core will be designated A02-SD1-006-012.

QAPP Worksheet #27
Sample Custody Requirements (Continued)

Field Duplicates

Field duplicate samples will be collected following the same procedures as the collection of samples for chemical and radiochemical analyses. One field duplicate sample will be collected for every 20 field samples. The following naming convention will be used for field duplicate samples:

- SD-00 to indicate a duplicate sample;
- Three-character alpha-numeric designation of the coring location; and
- Three digits to indicate the depth to the top of the sample interval in inches.

For example, a duplicate sample collected at location B01-SD-024-030 would be designated SD-00-B01-024.

Matrix Spike/Matrix Spike Duplicate Samples

Matrix spike/matrix spike duplicate (MS/MSD) samples will be generated by the laboratory. The laboratory will be instructed to generate the MS/MSD from sample material collected from this project for each SDG analyzed.

Rinsate Blanks

Rinsate blanks will be numbered by a unique 12-character string, as follows:

- Two characters to signify a rinsate blank (RB)
- Eight characters to describe the date using a four-digit year, two-digit month, two-digit day (e.g., YYYYMMDD).

For example, a rinsate blank collected on December 31, 2011 would be designated RB20111231.

QAPP Worksheet #27
Sample Custody Requirements (Continued)

Field Documentation Procedures

Pertinent field information will be recorded in a logbook and/or an appropriate form (SOP 7, Appendix A) in black, ballpoint pen. The field forms may be replaced with a personal data assistant (PDA) and/or an electronic field database. Every form in SOP 7 includes a key that describes each required entry. Logbook entries will be factual and observational (i.e., no speculation or opinion), and will not contain any personal information or non-project-related entries. Separate and dedicated logbooks will be kept for different operations running concurrently (e.g., core collection onboard the vessel, core processing at the Sample Processing Area); individual tasks making up each operation will be maintained in the same logbook, if possible. The cover and binding of each logbook will be labeled to identify the operation and dates included within the logbook; each page in the logbook will be consecutively numbered.

A page header will appear on the first page of each day's notes in the logbook, and activities for each day will be recorded on a new page. The page header will include:

- name of author and other personnel onsite (and affiliated organization if applicable)
- date
- time of arrival
- current weather and tidal conditions, and weather forecast for the day

An abbreviated header, limited to the date, will appear at the top of each additional page for the active date. Field forms (SOP 6, Appendix A) will require similar header information.

Field activities and other events pertinent to the field activities will be documented in chronological order. Times will be recorded using 24-hour notation for each entry. At a minimum, documentation in a logbook will include the following:

- names of visitor(s) to the work location being documented in the log, including time of arrival and departure, the visitor's affiliation, and reason for visit
- summary of project-related communications, including names of people involved and time
- time daily work commences and ceases
- start and stop times of new tasks
- start and stop times of breaks
- safety or other monitoring data, including units with each measurement
- deviations from scope of work
- progress updates
- problems/delays encountered
- unusual events
- signature or initials of author on every page

A single line will be drawn through incorrect entries and the corrected entry written next to the original strikeout.
Strikeouts are to be initialed and dated by the originator.

QAPP Worksheet #27
Sample Custody Requirements (Continued)

If there are additional lines on the page at the end of the day's activities, a line will be drawn through the empty space, initialed, and dated, leaving no room for additional entries.

The logbook will cross-reference information documented in the field forms.

Photographs will be identified in the logbook by a unique numbering system. If photographs are collected by a digital camera, the file number as well as the photograph number will accompany the description of the photograph in the logbook. At a minimum, the time the photograph was taken, the general location, a brief description, and the photographer's name will be recorded. Additional information may include: Differential Global Positioning System (DGPS) coordinates, direction the photographer was facing, and/or weather conditions. If necessary, an object will be included to indicate the scale of the object in the photograph.

Additional Requirements for Field Activities

Five field forms will be used to ensure proper documentation of field information is obtained in a consistent manner:

- Daily Activity Log – Provides a summary of daily vessel logistics during the sediment marker investigation field activities, including personnel present, equipment used, and weather conditions.
- Core Collection Form – Provides a summary of cores attempted and collected during each field day.
- Individual Core Collection Form – Provides core-specific information such as penetration and recovery measured during core collection. The Individual Core Collection Form also serves as the chain of custody for the core as it is transported from the coring vessel to the Sample Processing Area.
- Core Lithology/Description Form – Provides a lithological description of a core observed during sample processing.
- Sample Processing Form – Provides core-specific information on sample segmentation.

QAPP Worksheet #27
Sample Custody Requirements (Continued)

Logbooks, field forms, and chain of custody forms will be filed according to the FSIWP.

Logbooks that are taken offsite from the field offices will be photocopied and filed at the end of each day to mitigate against the loss of historical entries should the logbook be lost in the field.

Field data forms and chain of custody forms will be filed once they have been completed and distributed (if necessary), or at the end of each field day.

Distribution of daily forms will be performed according to the needs of the project team and at the direction of the Field Team Leader or designee.

Upon completion of sampling and transfer of samples to the shipping company or courier, copies of the signed chains of custody will be faxed to the Project Manager, appropriate analytical laboratory contact, and the data validator. Copies of these documents will also be maintained at the field office in a labeled three-ring binder in reverse chronological order.

The integrity of samples collected for analysis will be ensured and the samples continuously tracked in the Sample Processing Area and while in transit to the laboratory by use of the following procedures .

- The Sample Processing Area will be secured (locked) with limited access.
- Individual sample bottles will be properly labeled and securely sealed before being placed in the container for shipment to the laboratory.
- Pertinent information will be entered on the chain of custody form in the field.
- The chain of custody form must include the following, as required by guidance in SW-846, Test Methods for Evaluating Solid Waste (USEPA, 1993): 1) project name; 2) signatures of samplers; 3) sample number, date and time of collection; and grab or composite sample designation; 4) signatures of individuals involved in sample transfer; and 5) if applicable, the air bill or other shipping number.
- The completed chain of custody form will be signed, dated, enclosed in a sealable plastic bag and placed in the container prior to shipment. A copy of completed chain of custody form will be retained by field personnel and stored in a dedicated binder. Additional copies will be distributed as follows:
    - a copy will be faxed or emailed to the Project Manager or designee
    - a copy will be faxed or emailed to the data validator
    - a copy will be faxed or emailed to the lab manager/client service representative at each laboratory being used

QAPP Worksheet #27
Sample Custody Requirements (Continued)

Transfer of Custody and Shipment Procedures

Sample packaging and shipping will be done in accordance with applicable regulations, as described below.

- After filling a sample container, wipe clean with a paper towel (including jar threads), affix cap, complete the sample label and affix to container, then securely seal both cap and label with clear tape
- Seal each sample container inside a sealable plastic bag, then add an additional bag (i.e., double-bag the container).
- Place samples on ice or similar chilling source immediately after collection.
- Transfer the samples to a plastic-lined ice chest which will be used as a shipping container. Use inert packaging material (e.g., cardboard, vermiculite, etc.) to cushion the samples and minimize the potential for breakage. Seal the drains on the ice chest (if present) with shipping tape or plug the drains with silicone sealant or a similar inert substance.
- Ice chests will contain ice or similar chilling sources sufficient to maintain a temperature of 4° Celsius (°C) inside the cooler during transport. Use sufficient ice to accommodate 1 extra day delay (i.e., 2 days) during sample shipment. A temperature blank provided by the analytical laboratory with each cooler will be included in the shipment.
- Complete sample tracking documentation as described in SOP 8, Section6, Appendix A, and place the documents in a sealable plastic bag inside the ice chest, taped to the inside of the lid. Prior to sealing for shipment, check the list of samples against the container contents to verify the presence of each sample listed on the chain of custody.
- Secure chest lid with shipping tape by covering the entire seal with tape. Complete information on the custody seal and affix the custody seal over the taped seal.
- Transport the shipping container directly to the laboratory, the laboratory courier, or to the overnight carrier for overnight delivery.
- Once a core has been opened, sediment samples will be shipped by close of the same day.
- Rinsate blank samples will also be shipped by close of the same day with the appropriate SDG.

QAPP Worksheet #27
Sample Custody Requirements (Continued)

From the time of collection through transportation, the handling of samples will follow chain of custody procedures. Completed and signed Individual Core Collection Forms will be provided by the samplers to the Sample Processing Area personnel when relinquishing the collected cores for sample processing. The Sample Processing Area personnel will sign the Individual Core Collection Form accepting custody of the cores.

- The completed chain of custody form will be signed, dated, enclosed in a sealable plastic bag and placed in the container prior to shipment. A copy of both the Individual Core Collection Form and the chain of custody form will be retained by field personnel and stored in a dedicated binder. Additional copies will be distributed as follows:
    - a copy will be faxed or emailed to the Project Manager or designee
    - a copy will be faxed or emailed to the data validator
    - a copy will be faxed or emailed to the lab manager/client service representative at each laboratory being used

2) Laboratory Custody Procedures

Upon receipt at the laboratory, the designated laboratory sample custodian shall sign the chain of custody form indicating receipt of the incoming field samples. The samples shall be checked against the chain of custody form upon arrival at the laboratory. The receiving personnel will enter all arriving samples into a laboratory logbook. Any discrepancies between the samples and the chain of custody form(s), or any evidence of tampering with the shipping container or the custody seal will be immediately reported to the Project Manager. The sample custodian will immediately check the temperature of the cooler upon arrival at the laboratory and record the measured temperature on the chain of custody form and in a laboratory logbook. The laboratory sample custodian will examine the condition, preservation, and accompanying documentation of submitted samples prior to approval and formal acceptance by the laboratory. Any sample, preservation, or documentation discrepancies (i.e., broken sample container, improper preservation, unacceptable cooler temperature, inadequate sample volume, or poor documentation) will be resolved before the sample is approved and formally accepted for analysis. Required acceptance data will be recorded and documented in the laboratory sample log and Laboratory Information Management System. The sample will be labeled with a unique laboratory identification and placed in the secure sample storage area prior to distribution to the appropriate analyst(s).

QAPP Worksheet #27
Sample Custody Requirements (Continued)

The analyst(s) must sign out samples from the Laboratory Sample Custodian by entering their initials, date, and time of sample removal into a log or logbook. Any time the sample or extract is removed from or returned to the refrigerator, the pertinent information (analyst initials, date, and time) will be recorded into the log or logbook. The sample or extract will remain at the laboratory facility for at least 6 months after sample collection. Samples are to be stored under conditions appropriate for a given analytical group. These conditions are described in Worksheets #19. Samples and/or sample residual material, including jars and containers, will be returned to the Diamond Alkali Superfund Site by the laboratories, but only after the sample archival period expires. No less than 30 days prior to shipment, the laboratory will contact Tierra, in writing, to request final instructions on return shipment of samples and/or sample residual material, including jars and containers, to the Diamond Alkali Superfund Site. Under no circumstances will the laboratories dispose of samples and/or sample residual material, including jars and containers, without the express, written direction of Tierra Solutions, Inc. or their representatives. Residual material will later be containerized at the Diamond Alkali Superfund Site.

3) Final Documentary File Custody Procedures

Hard copies of project documentation and data will be placed in the project file, parts of which will exist in several locations, including:

- ENVIRON International Corporation, Princeton, New Jersey
- Environmental Data Services, Ltd., Pittsburgh, Pennsylvania
- Tierra Solutions, Inc., East Brunswick, New Jersey.

Such files will be maintained in secure locations within each facility. Duplicate copies of pertinent field-related correspondence/documentation will be maintained at the field office during field operations. Once such field operations have been completed, this documentation will be transferred to the project file.

Upon completion of the data validation process, project documents and records listed in Worksheets 29-1 through 29-4 will also be stored in the project file. At such time that it is deemed appropriate to archive the project file, either in parts or in its entirety, files will be boxed and shipped off-site to a secure document storage facility. The assigned barcode identifier for each box being archived will be logged into a tracking spreadsheet, including a brief description of the contents of the box. Archived boxes will be retrieved from the storage facility if/when necessary using the logged barcode identifier.

QAPP Worksheet #28-1
Sediment Field Quality Control Samples

Matrix	Sediment
Analytical Group	HCX, PCDDs/PCDFs,Cs-137[a]
Concentration Level	Low
Sampling SOP	SOP-3, SOP-4, and SOP-5
Analytical Method/SOP Reference	L-1, L-2, L-3
Field Sampling Organization	ENVIRON
Analytical Organization	Vista Analytical, ALS Environmental
Number of Samples Collected[b]	61

QC Sample	Frequency Number	Action	Data Quality Indicator	Measurement Performance Criteria
Subsample Field Duplicates	1 field duplicate will be collected at a frequency of 1 per sample delivery group not to exceed 1 per 20 samples per matrix and per method.	Associated data will be critically assessed to determine the impact to data quality.	Precision	RPD ≤50% when target is detected in both the sample and the field duplicate sample at >5X PQL, or concentrations differ by less than 2X the PQL when detects are <5X PQL for the duplicate pair.
Rinsate Blanks[c]	1 per decontamination event (not to exceed 1 per day) and 1 pre project on core liner as a lot check.	Associated data will be critically assessed to determine the impact to data quality.	Accuracy/Bias Contamination	No target compounds ≥PQL

QAPP Worksheet #28-1
Sediment Field Quality Control Samples (Continued)

Notes:
[a] Cs-137 is provided as an optional analysis that may be performed at the project team's discretion.
[b] Represents the number of sediment samples collected for analysis initially. Additional core segments may be analyzed at the project team's discretion. If additional core segments are analyzed quality control samples will also be evaluated as described in this worksheet.
[c] Rinsate blanks are not required for Cs-137.

Cs-137 = Cesium-137
HCX = 1,2,4,5,7,8-hexachloro(9H)xanthene
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
PQL = project quantitation limit
QC = quality control
RPD = relative percent difference
SOP = Standard Operating Procedure

QAPP Worksheet #28-1
Field Quality Control Samples (Continued)

Description of Terms:

Subsample Field Duplicate

Subsample field duplicates check for precision in the sampling technique as well as changes that may arise during sample transportation.

Field duplicates are samples collected from the same homogenized material as the original sample, which is assigned a separate and discrete sample number.

Rinsate Blank

Rinsate blanks check for sample contamination caused by reuse of decontaminated sampling equipment as well as the sampling process and transportation.

Rinsate blanks are samples collected by pouring "analyte-free" de-ionized water or solvent, whichever is appropriate to the contaminants of interest, over the sampling equipment after it has been cleaned in the field. Rinsate blanks are collected and analyzed for each type of equipment used each day a decontamination event is carried out; not to exceed one per day. For dedicated sampling equipment, such as core liners, that are not reused, rinsate blanks are collected once prior to initiation of field sampling activities. One rinsate blank will be collected from each type of dedicated sampling equipment to be used (core liners).

QAPP Worksheet #28-2a
Rinsate Blank Laboratory Quality Control Samples

Matrix	Rinsate Blank
Analytical Group	HCX
Concentration Level	Low
Sampling SOP	SOP-1
Analytical Method/ SOP Reference	L-1
Field Sampling Organization	ENVIRON
Analytical Organization	Vista Analytical
No. of Samples Collected	7

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Ongoing Precision and Recovery	1 per extraction batch[a]	HCX recovery (50-150%)	The laboratory should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-digest/re-distill and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	HCX recovery (50-150%)
Method Blanks	1 per extraction batch[a]	No target compound ≥ PQL	The laboratory should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-analyze affected samples. If insufficient sample is available, qualify data as needed.	Accuracy/Bias Contamination	No target compound ≥ PQL

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a
Rinsate Blank Laboratory Quality Control Samples (Continued)

Matrix	Rinsate Blank
Analytical Group	HCX
Concentration Level	Low
Sampling SOP	SOP-1
Analytical Method/SOP Reference	L-1
Field Sampling Organization	ENVIRON
Analytical Organization	Vista Analytical
No. of Samples Collected	7

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Initial Calibration	At initial setup or when corrective action is taken, which may change calibration, per L-1	Per L-1	Investigate and recalibrate, if necessary; refer to L-1	Accuracy/Bias	Per L-1
Calibration Verification	Prior to every 12-hour period, but following Column Performance Solution and at end of 12-hour period, per L-1	Per L-1	Investigate and recalibrate, if necessary; refer to L-1	Accuracy/Bias	Per L-1
Labeled Compound Spike	1 per sample	Per L-1	The laboratory should review their protocols and correct any that may have caused exceedance of QC acceptance limits; refer to L-1	Accuracy/Bias	Per L-1
Labeled Internal Standard	1 per sample	Per L-1	The laboratory should review their protocols and correct any that may have caused exceedance of QC acceptance limits; refer to L-1	Accuracy/Bias	Per L-1

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a
Rinsate Blank Laboratory Quality Control Samples (Continued)

Matrix	Rinsate Blank
Analytical Group	PCDDs/PCDFs
Concentration Level	Low
Sampling SOP	SOP-1
Analytical Method/SOP Reference	L-2
Field Sampling Organization	ENVIRON
Analytical Organization	Vista Analytical
No. of Samples Collected	7

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Ongoing Precision and Recovery	1 per extraction batch[a]	All target compound concentrations must fall within range provided in Table 6 of L-2	The laboratory should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-digest/re-distill and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	All target compound concentrations must fall within range provided in Table 6 of L-2
Method Blanks	1 per extraction batch[a]	No target compounds ≥ PQL	The laboratory should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a
Rinsate Blank Laboratory Quality Control Samples (Continued)

Matrix	Rinsate Blank
Analytical Group	PCDDs/PCDFs
Concentration Level	Low
Sampling SOP	SOP-1
Analytical Method/SOP Reference	L-2
Field Sampling Organization	ENVIRON
Analytical Organization	Vista Analytical
No. of Samples Collected	7

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Initial Calibration	At initial setup or when corrective action is taken, which may change calibration, per L-2	Per L-2	Investigate and recalibrate, if necessary; refer to L-2	Accuracy/Bias	Per L-2
Calibration Verification	Prior to every 12-hour period, but following Column Performance Solution and at end of 12-hour period, per L-2	Per L-2	Investigate and recalibrate, if necessary; refer to L-2	Accuracy/Bias	Per L-2
Labeled Compound Spike	1 per sample	Per L-2	The laboratory should review their protocols and correct any that may have caused exceedance of QC acceptance limits; refer to L-2	Accuracy/Bias	Per L-2
Labeled Internal Standard	1 per sample	Per L-2	The laboratory should review their protocols and correct any that may have caused exceedance of QC acceptance limits; refer to L-2	Accuracy/Bias	Per L-2

See the last page of Worksheet #28-2a for a description of footnotes.

QAPP Worksheet #28-2a
Field Blank/Rinse Blank Laboratory Quality Control Samples (Continued)

Notes:
[a] A batch is defined as a group of up to 20 samples of the same matrix, prepared at the same time, using the same procedure.

HCX = 1,2,4,5,7,8-hexachloro(9H)xanthene
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
PQL = project quantitation limit
QC = quality control
RPD = relative percent difference
SOP = Standard Operating Procedure
TBD = to be determined
% = percent

QAPP Worksheet #28-2b
Sediment Laboratory Quality Control Samples

Matrix	Sediment
Analytical Group	HCX
Concentration Level	Low
Sampling SOP	SOP-3, SOP-4, and SOP-5
Analytical Method/ SOP Reference	L-1
Field Sampling Organization	ENVIRON
Analytical Organization	Vista Analytical
No. of Samples Collected[a]	61

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Method Blanks	1 per extraction batch[b]	No target compound ≥ PQL	The laboratory should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-analyze affected samples. If insufficient sample is available, qualify data as needed.	Accuracy/Bias Contamination	No target compound ≥ PQL

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b
Sediment Laboratory Quality Control Samples (Continued)

Matrix	Sediment
Analytical Group	HCX
Concentration Level	Low
Sampling SOP	SOP-3, SOP-4, and SOP-5
Analytical Method/ SOP Reference	L-1
Field Sampling Organization	ENVIRON
Analytical Organization	Vista Analytical
No. of Samples Collected[a]	61

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Matrix Spike	1 per extraction batch[b]	HCX recovery (50-150%)	The laboratory should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	HCX recovery (50-150%)
Matrix Spike Duplicate	1 per extraction batch[b]	RPD ≤20%	The laboratory should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Precision	RPD ≤20%

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b
Sediment Laboratory Quality Control Samples (Continued)

Matrix	Sediment
Analytical Group	HCX
Concentration Level	Low
Sampling SOP	SOP-3, SOP-4, and SOP-5
Analytical Method/ SOP Reference	L-1
Field Sampling Organization	ENVIRON
Analytical Organization	Vista Analytical
No. of Samples Collected[a]	61

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Ongoing Precision and Recovery	1 per extraction batch[b]	HCX recovery (50-150%)	The laboratory should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	HCX recovery (50-150%)
Initial Calibration	At initial setup or when corrective action is taken, which may change calibration per L-1	Per L-1	Investigate and recalibrate, if necessary; refer to L-1	Accuracy/Bias	Per L-1
Calibration Verification	Prior to every 12-hour period, but following Column Performance Solution and at end of 12-hour period per L-1	Per L-1	Investigate and recalibrate, if necessary; refer to L-1	Accuracy/Bias	Per L-1
Labeled Internal Standard	1 per sample	Per L-1	The laboratory should review their protocols and correct any that may have caused exceedance of QC acceptance limits; refer to L-1	Accuracy/Bias	Per L-1

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b
Sediment Laboratory Quality Control Samples (Continued)

Matrix	Sediment
Analytical Group	PCDDs/PCDFs
Concentration Level	Low
Sampling SOP	SOP-3, SOP-4, and SOP-5
Analytical Method/SOP Reference	L-2
Field Sampling Organization	ENVIRON
Analytical Organization	Vista Analytical
No. of Samples Collected[a]	61

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
Method Blanks	1 per extraction batch[b]	No target compounds ≥ PQL		The laboratory should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias Contamination	No target compounds ≥PQL	
Matrix Spike	1 per extraction batch[b]	**Compound** All target analytes	**% Recovery** 60-140	The laboratory should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	**Compound** All target analytes	**% Recovery** 60-140

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b
Sediment Laboratory Quality Control Samples (Continued)

Matrix	Sediment
Analytical Group	PCDDs/PCDFs
Concentration Level	Low
Sampling SOP	SOP-3, SOP-4, and SOP-5
Analytical Method/SOP Reference	L-2
Field Sampling Organization	ENVIRON
Analytical Organization	Vista Analytical
No. of Samples Collected[a]	61

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits		Corrective Action	Data Quality Indicator	Measurement Performance Criteria	
		Compound	**RPD**			**Compound**	**RPD**
Matrix Spike Duplicate	1 per extraction batch[b]	All target analytes	<50	The laboratory should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Precision	All target analytes	<50
Ongoing Precision and Recovery	1 per extraction batch[b]	All target compound concentrations must fall within range provided in Table 6 of L-2		The laboratory should review their protocols and correct any that may have caused exceedance of the QC acceptance limits. If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy/Bias	All target compound concentrations must fall within range provided in Table 6 of L-2	

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b
Sediment Laboratory Quality Control Samples (Continued)

Matrix	Sediment
Analytical Group	PCDDs/PCDFs
Concentration Level	Low
Sampling SOP	SOP-3, SOP-4, and SOP-5
Analytical Method/SOP Reference	L-2
Field Sampling Organization	ENVIRON
Analytical Organization	Vista Analytical
No. of Samples Collected[a]	61

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Initial Calibration	At initial setup or when corrective action is taken, which may change calibration per L-2	Per L-2	Investigate and recalibrate, if necessary; refer to L-2	Accuracy/Bias	Per L-2
Calibration Verification	Prior to every 12-hour period, but following Column Performance Solution and at end of 12-hour period per L-2	Per L-2	Investigate and recalibrate, if necessary; refer to L-2	Accuracy/Bias	Per L-2
Labeled Compound Spike	1 per sample	Per L-2	The laboratory should review their protocols and correct any that may have caused exceedance of QC acceptance limits; refer to L-2	Accuracy/Bias	Per L-2
Labeled Internal Standard	1 per sample	Per L-2	The laboratory should review their protocols and correct any that may have caused exceedance of QC acceptance limits; refer to L-2	Accuracy/Bias	Per L-2

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b
Sediment Laboratory Quality Control Samples (Continued)

Matrix	Sediment
Analytical Group	Cs-137[c]
Concentration Level	Low
Sampling SOP	SOP-3, SOP-4, and SOP-5
Analytical Method/SOP Reference	L-3
Field Sampling Organization	ENVIRON
Analytical Organization	ALS Environmental
No. of Samples Collected[a]	0

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Data Quality Indicator	Measurement Performance Criteria
Laboratory Duplicate	1 per preparation batch[b]	Activity reported for each of the two duplicate samples should differ by no more than 2-sigma bands or mean difference value between results reported of less than 3.	If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Precision	Activity reported for each of the two duplicate samples should differ by no more than 2-sigma bands or mean difference value between results reported of less than 3.
Laboratory Control Sample	1 per preparation batch[b]	Cs-137 recovery (70-130%)	If sufficient field sample is available, re-extract and re-analyze affected samples. If insufficient sample is available, re-analyze extracts. Qualify data as needed.	Accuracy	Cs-137 recovery (70-130%)

See the last page of Worksheet #28-2b for a description of footnotes.

QAPP Worksheet #28-2b
Sediment Laboratory Quality Control Samples (Continued)

Notes:
[a] Represents the number of sediment samples collected for analysis initially. Additional core segments may be analyzed at the project team's discretion. If additional core segments are analyzed quality control samples will also be evaluated as described in this worksheet.
[b] A batch is defined as a group of up to 20 samples of the same matrix, prepared at the same time, using the same procedure.
[c] Cs-137 is provided as an optional analysis that may be performed at the project team's discretion.

Cs-137 = Cesium-137
HCX = 1,2,4,5,7,8-hexachloro(9H)xanthene
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
PQL = project quantitation limit
QC = quality control
RPD = relative percent difference
SOP = Standard Operating Procedure

QAPP Worksheet #29-1
Project Documents and Records

Sample Collection Documents and Records	On-Site Analysis Documents and Records	Off-Site Analysis Documents and Records	Data Assessment Documents and Records
Airbills Chain of Custody Records Core Chain-of-Custody Form Core Collection Form Individual Core Collection Form Core Lithology/Description Custody Seal Daily Activity Log Decontamination/Rinse Blank Logbook	Air Monitoring Log for Core Collection Air Monitoring Log for Core Processing Employee and Visitor Log Equipment Calibration and Maintenance Log for Core Processing Refrigeration Unit Sign-in Sheet FSIWP/QAPP Revision #0 QAPP Water Quality Meter Bench Log Other Field Instrument Calibration Records Field Instrument Sample Result Recording	Hardcopy data package as specified in Worksheet #29-2. Electronic data deliverable as specified in Worksheet #29-4.	Laboratory QA Plans Laboratory Certifications MDL Study Information Data Validation Reports Corrective Action Reports - Field and Laboratory

See the last page of Worksheet #29-1 for a description of footnotes.

QAPP Worksheet #29-1
Project Documents and Records (Continued)

Sample Collection Documents and Records	On-Site Analysis Documents and Records	Off-Site Analysis Documents and Records	Data Assessment Documents and Records
Photo Logbook for Core Collection			
Photo Logbook for Core Processing			
Pre-Printed Sample Label			
Sample Processing Form			
Custody Seal			
SDG Tracking Log			
Bills of Lading			

Notes:

FSIWP/QAPP = Focused Sediment Investigation Work Plan/Quality Assurance Project Plan
MDL = method detection limit
QA = quality assurance
SDG = sample delivery group

QAPP Worksheet #29-2
Required Analytical Chemistry Data Deliverable Elements

Data Deliverable Elements	HCX	PCDDs/ PCDFs	Cs -137
• **INVENTORY SHEET** (Organic Form DC-2 and/or Radiochemistry sample identification sheet)	X	X	X
• **NARRATIVE** (Organic and Radiochemistry)	X	X	X
• **SHIPPING/RECEIVING DOCUMENTS AND INTERNAL LABORATORY CHAIN OF CUSTODY RECORDS:**			
Airbills	X	X	X
Chain of Custody records/forms (Traffic Report)	X	X	X
Miscellaneous shipping/receiving records	X	X	X
Internal laboratory sample transfer records and tracking sheets	X	X	X
• **SAMPLE DATA:**			
Tabulated Summary Form for Field Sample Results (Organic and Inorganic Form I, Radiochemistry)	X	X	X
All related raw data for radiochemistry			X
• **STANDARDS DATA:**			
Method Detection Limit Study tabulated summary form	X	X	
Summarized gamma spectroscopy instrument initial calibrations			X
Summarized gamma spectroscopy instrument continuing calibration			X

See the last page of Worksheet #29-2 for a description of footnotes.

QAPP Worksheet #29-2
Required Analytical Chemistry Data Deliverable Elements (Continued)

Data Deliverable Elements	HCX	PCDDs/PCDFs	Cs -137
• **QC DATA:**			
Quality control charts (efficiency and background) for each detector used			X
Summarized QC sample results for gamma spectroscopy			X
QC raw data	X	X	X
• **METADATA:**			
Sample preparation/extraction and logbook pages	X	X	X
Sample analysis gamma spectroscopy logbook			X
Sample analysis run log and logbook pages	X	X	X
Standards preparation logbook pages	X	X	X
QC Sample preparation logbook pages	X	X	X
Date of Sample preparation and analysis	X	X	X
Sample Holding Temperature Documentation	X	X	X
Sample Preservation Verification Documents	X	X	X
• **MISCELLANEOUS DATA:**			
Percent solids determination log	X	X	
Other records (e.g., telephone communication log)	X	X	X

See the last page of Worksheet #29-2 for a description of footnotes.

QAPP Worksheet #29-2
Required Analytical Chemistry Data Deliverable Elements (Continued)

Data Deliverable Elements	HCX	PCDDs/PCDFs	Cs-137
• **HIGH RESOLUTION MASS SPECTROMETRY:**			
Analysis Data Sheet	X	X	
Confirmation analysis data sheet	X	X	
Clean-up standard recoveries	X	X	
Tabulated relative retention times for samples	X	X	
SICPs for each sample	X	X	
Method blank summarized results	X	X	
SICPs for each method blank	X	X	
Mass spectrometer resolutions demonstration SICPs for each analysis shift	X	X	
SICPs for 12-hour continuing calibration standard	X	X	
Gas chromatograph resolution demonstration SICPs for each 12-hour sequence	X	X	
Initial Calibration Relative Retention Times	X	X	
Initial Calibration Response Factors	X	X	
Initial Calibration Ion Abundance Ratios	X	X	
SICPs for the Initial Calibration	X	X	
Initial Precision and Recovery	X	X	
Ongoing Precision and Recovery	X	X	
MS/MSD Results and Spiked Level Summary	X	X	

See the last page of Worksheet #29-2 for a description of footnotes.

QAPP Worksheet #29-2
Required Analytical Chemistry Data Deliverable Elements (Continued)

Notes:

( ) = form number; refer to CLP SOW forms if CLP is used
CLP = Contract Laboratory Program
CRDL = contract required detection limit
GC = gas chromatography
GC/MS = gas chromatography/spectrometry
HCX = 1,2,4,5,7,8-hexachloro(9H)xanthene
MS/MSD = matrix spike/matrix spike duplicate
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
QC = quality control
RT = retention time
SICPs = selected ion current profiles
SOW = statement of work

QAPP Worksheet #29-3
Standard Laboratory Data Qualifiers

The laboratory qualifiers and their stated definitions provided below will be used by the laboratories exclusively when reporting sample results for the Quality Assurance Project Plan.

Chemical Analyses Laboratory Qualifiers	
Qualifier	**Description**
B	Organics – The associated analyte was also detected in the method blank.
D	The organic analyte was quantitated from a diluted analysis.
E	Organics – The associated compound concentration exceeded the calibration range of the instrument.
G	Organic data indicated the presence of a compound that meets the identification criteria; the result is below the PQL but above the method detection limit (MDL) or estimated detection limit (EDL), where appropriate.
U	The analyte was analyzed for, but was not detected above the reported sample quantitation limit.
S	Inorganics - The reported value was determined by Method of Standard Additions (MSA).
I	The laboratory indicated the presence of an interference during the sample analysis.

Other Data Reporting Requirements:

- Only analytical data that are validated (see Worksheets #34, #35 and #36) will be reported.
- Organic analytes detected below the PQL, but above the MDL/EDL, will be reported with a "G" flag, and organic analytes detected below the PQL and MDL/EDL as non-detects at the PQL.

QAPP Worksheet #29-3
Standard Laboratory Data Qualifiers (Continued)

Radiochemistry Analyses Laboratory Qualifiers	
Qualifier	**Description**
G	Measured sample activity is larger than the critical value but less than the minimum detectable concentration.
U	Measured sample activity is less than the critical value and therefore is not statistically positive.

QAPP Worksheet #29-4
Example Format for Electronic Loading of Laboratory Files

ANALYTE	UNITS	MW-1[a]	LQ	VQ	MW-2[a]	LQ	VQ	MW-3[a]	LQ	VQ
Phenol	µg/kg	500	U		500	U		500	U	
bis(2-Chloroethyl)ether	µg/kg	110	U		110	U		110	U	
2-Chlorophenol	µg/kg	110	U		110	U		110	U	
1,3-Dichlorobenzene	µg/kg	110	U		110	U		110	U	
1,4-Dichlorobenzene	µg/kg	250	U		250	U		250	U	
1,2-Dichlorobenzene	µg/kg	110	U		110	U		110	U	
2-Methylphenol	µg/kg	250	U		250	U		250	U	
2,2'-oxybis(1-Chloropropane)	µg/kg	2,500	U		2,500	U		2,500	U	
4-Methylphenol	µg/kg	750	U		750	U		750	U	
N-Nitroso-di-n-propylamine	µg/kg	250	U		250	U		250	U	
Hexachloroethane	µg/kg	250	U		250	U		250	U	
Nitrobenzene	µg/kg	250	U		250	U		250	U	
Isophorone	µg/kg	250	U		250	U		250	U	
2-Nitrophenol	µg/kg	110	U		110	U		110	U	
2,4-Dimethylphenol	µg/kg	110	U		110	U		110	U	
bis(2-Chloroethoxy)methane	µg/kg	110	U		110	U		110	U	
2,4-Dichlorophenol	µg/kg	110	U		110	U		110	U	
1,2,4-Trichlorobenzene	µg/kg	110	U		110	U		110	U	
Naphthalene	µg/kg	110	U		110	U		110	U	
4-Chloroaniline	µg/kg	110	U		110	U		110	U	
Hexachlorobutadiene	µg/kg	110	U		110	U		110	U	
4-Chloro-3-methylphenol	µg/kg	110	U		110	U		110	U	
2-Methylnaphthalene	µg/kg	110	U		110	U		110	U	

Notes:

[a] Example sample IDs

LQ = laboratory qualifiers
µg/kg = micrograms per kilogram
VQ = validation qualifiers

QAPP Worksheet #30
Analytical Services

Matrix: Sediment
Concentration: Low

Analytical Group	Sample Locations/ID Numbers	Analytical SOP	Data Package[a] Turnaround Time	Laboratory/Organization	Backup Laboratory/Organization
HCX	As specified in Worksheets #18	L-1	40 days	Vista Analytical Laboratory	TBD
PCDDs/PCDFs	As specified in Worksheets #18	L-2	40 days	Vista Analytical Laboratory	TBD
Cs-137	As specified in Worksheets #18	L-3	45 days	ALS Environmental	TBD

Notes:

[a] Turnaround time based on day the last sample in the sample delivery group is received by laboratory.

Cs-137 = Cesium-137
HCX = 1,2,4,5,7,8-hexachlor(9H)xanthene
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans
SOP = Standard Operating Procedure
TBD = to be determined

QAPP Worksheet #31
Planned Project Assessment

Assessment Type	Frequency	Internal or External	Organization Performing Assessment	Person(s) Responsible for Performing Assessment (Title and Organization Affiliation)	Person(s) Responsible for Responding to Assessment Findings (Title and Organizational Affiliation)	Person(s) Responsible for Identifying and Implementing Corrective Actions (Title and Organizational Affiliation)	Person(s) Responsible for Monitoring Effectiveness of Corrective Action (Title and Organizational Affiliation)
Field Readiness Review	1 prior to sampling startup	Internal	ENVIRON	Linda Hall Project Manager ENVIRON	John Pekala Field Team Leader ENVIRON	John Pekala Field Team Leader ENVIRON	Linda Hall Project Manager ENVIRON
Laboratory Readiness Review	1 prior to sampling startup	Internal	Vista Analytical Laboratory	Martha Maier Laboratory Project Manager Vista Analytical Laboratory El Dorado Hill, CA	Various Personnel Vista Analytical Laboratory El Dorado Hills, CA	Various Personnel Vista Analytical Laboratory El Dorado Hills, CA	Martha Maier Laboratory Project Manager Vista Analytical Laboratory El Dorado Hill, CA
Laboratory Readiness Review	1 prior to sampling startup	Internal	ALS Environmental	Julie Ellingson Laboratory Project Manager ALS Environmental Fort Collins, CO	Various Personnel ALS Environmental Fort Collins, CO	Various Personnel ALS Environmental Fort Collins, CO	Julie Ellingson Laboratory Project Manager ALS Environmental Fort Collins, CO
Data Validation	All analytical data collected are validated[a]	External	Environmental Data Services, Ltd.	Diane Waldschmidt Quality Assurance Coordinator Environmental Data Services, Ltd.	Field and Laboratory Contractors	Field and Laboratory Contractors	Diane Waldschmidt Quality Assurance Coordinator Environmental Data Services, Ltd.
Internal Laboratory Audit	1 audit prior to use	Internal	Vista Analytical Laboratory	Rose Harrelson Quality Assurance Coordinator Vista Analytical Laboratory El Dorado Hill, CA	Various Personnel Vista Analytical Laboratory El Dorado Hills, CA	Various Personnel Vista Analytical Laboratory El Dorado Hills, CA	Diane Waldschmidt Quality Assurance Coordinator Environmental Data Services, Ltd.
Internal Laboratory Audit	1 audit prior to use	Internal	ALS Environmental	Robert DiRienzo Quality Assurance Coordinator ALS Environmental Fort Collins, CO	Various Personnel ALS Environmental Fort Collins, CO	Various Personnel ALS Environmental Fort Collins, CO	Diane Waldschmidt Quality Assurance Coordinator Environmental Data Services, Ltd.

Notes:

[a] All data collected will undergo full data validation as outlined in Worksheet #36.

QAPP Worksheet #32
Assessment Findings and Corrective Actions Responses

Assessment Type	Nature of Deficiencies Documentation	Individual(s) Notified of Findings (Name, Title, Organization)	Time frame of Notification	Nature of Corrective Action Response Documentation	Individual(s) Receiving Corrective Action Response (Name, Title, and Organization)	Time frame for Response
Field Readiness Review	Memo	John Pekala Field Team Leader ENVIRON	24 hours after review complete	Memo	Paul J. Brzozowski Project Coordinator Tierra Solutions, Inc.	Immediate
Laboratory Readiness Review	Memo	Martha Maier Laboratory Project Manger Vista Analytical Laboratory El Dorado Hill CA	24 hours after review complete	Memo	Paul J. Brzozowski Project Coordinator Tierra Solutions, Inc.	Immediate
Laboratory Readiness Review	Memo	Julie Ellingson Laboratory Project Manager ALS Environmental Fort Collins, CO	24 hours after review complete	Memo	Paul J. Brzozowski Project Coordinator Tierra Solutions, Inc.	Immediate
Data Validation[a]	Validation Reports	All of those listed above as impacted	40 days after receipt of laboratory and field deliverables	Resubmission of missing or corrected documents	Paul J. Brzozowski Project Coordinator Tierra Solutions, Inc.	1 week after request
Internal Laboratory Audit	Audit Report	Martha Maier Laboratory Project Manger Vista Analytical Laboratory El Dorado Hill CA	As required by laboratory QMP	Memo or as required by laboratory QMP	Diane Waldschmidt Quality Assurance Coordinator Environmental Data Services, Ltd.	As required by laboratory QMP
Internal Laboratory Audit	Audit Report	Julie Ellingson Laboratory Project Manager ALS Environmental Fort Collins, CO	As required by laboratory QMP	Memo or as required by laboratory QMP	Diane Waldschmidt Quality Assurance Coordinator Environmental Data Services, Ltd.	As required by laboratory QMP

Notes:

[a] All data collected will undergo full data validation (Worksheet #s 35 and 36).

QMP - quality management plan

QAPP Worksheet #33
QA Management Reports

Type of Report	Frequency (daily, weekly, monthly, quarterly, annually, etc.)	Projected Delivery Date(s)	Person(s) Responsible for Report Preparation (Title and Organizational Affiliation)	Report Recipient(s) (Title and Organizational Affiliation)
Internal Laboratory Audit Report	1 report per audit conducted	Within 30 days of audit completion	Martha Maier Vista Analytical El Dorado, Ca	Paul J. Brzozowski Project Coordinator Tierra Solutions, Inc.
Internal Laboratory Audit Report	1 report per audit conducted	Within 30 days of audit completion	Julie Ellingson ALS Environmental Fort Collins, CO	Paul J. Brzozowski Project Coordinator Tierra Solutions, Inc.
Data Validation Reports	1 per sample delivery group, per analytical group	Within 40 days of receipt of final deliverables in the sample delivery group	Diane Waldschmidt Quality Assurance Coordinator Environmental Data Services, Ltd.	Paul J. Brzozowski Project Coordinator Tierra Solutions, Inc.
Data Usability Assessment Report	1 after completion of validation task	Within 40 days of validation completion	Diane Waldschmidt Quality Assurance Coordinator Environmental Data Services, Ltd.	Paul J. Brzozowski Project Coordinator Tierra Solutions, Inc.

Notes:

All data collected will undergo full data validation (Worksheets #35 and #36)

QAPP Worksheet #34
Verification (Step I) Process

VERIFICATION INPUT	DESCRIPTION	INTERNAL/ EXTERNAL	RESPONSIBLE FOR VERIFICATION (NAME, ORGANIZATION)
Chain-of-Custody and shipping forms	Chain-of-custody/requests for analysis forms and shipping documentation will be reviewed internally upon their completion and verified against the packed sample coolers they represent. The shipper's signature on the chain-of-custody should be initialed by the reviewer, a copy of the chain-of-custody retained in the site file, and the original and remaining copies taped inside each cooler for shipment. Chain-of-custody procedures are specified in SOP 8 – Containers, Preservation, Handling and Tracking of Samples for Analysis.	I/E	John Pekala ENVIRON Diane Waldschmidt Environmental Data Services, Ltd.
Field Notes	Field notes will be reviewed internally and placed in the project file.	I	John Pekala ENVIRON
Corrective Action Reports	Corrective Action Reports (when necessary) will be verified for completeness and signed by the Project Coordinator and Quality Assurance Coordinator. Corrective actions must also be communicated to appropriate field staff, as well as project review personnel.	I	Paul Brzozowski Tierra Solutions Inc. Diane Waldschmidt Environmental Data Services, Ltd.
Documentation of deviation from sample collection methods	Verify completeness and accuracy prior to distribution and placement in the project file. Communicate deviations to pertinent field staff, as well as project review personnel.	I	John Pekala ENVIRON Diane Waldschmidt Environmental Data Services, Ltd.
Onsite Field Testing	All onsite field test data will be reviewed against the FSIWP/QAPP requirements for completeness and accuracy based on the field calibration records	I	John Pekala ENVIRON
Field Standard Operating Procedures	Ensure that all sampling Standard Operating Procedures (SOPs) were followed	I	John Pekala ENVIRON
Field-generated electronic data deliverables	Verify completeness and accuracy prior to distribution and placement in the project file.	I	John Pekala ENVIRON

See the last page of Worksheet #34 for a description of footnotes.

QAPP Worksheet #34
Verification (Step I) Process (Continued)

VERIFICATION INPUT	DESCRIPTION	INTERNAL/ EXTERNAL	RESPONSIBLE FOR VERIFICATION (NAME, ORGANIZATION)
Identification of QC samples	Verify completeness and accuracy prior to distribution and placement in the project file.	I	John Pekala ENVIRON
Observed climatological condition recordings	Verify completeness and accuracy prior to distribution and placement in the project file.	I	John Pekala ENVIRON
Equipment decontamination records	Verify completeness and accuracy prior to distribution and placement in the project file.	I	John Pekala ENVIRON
Sampling equipment calibration logs	Verify completeness and accuracy prior to distribution and placement in the project file.	I	John Pekala ENVIRON
Field measurements documentation	Verify completeness and accuracy prior to distribution and placement in the project file.	I	John Pekala ENVIRON
Sample condition upon receipt and storage records	Chain of custody/requests for analysis forms and shipping documentation will be reviewed upon cooler receipt. The contents of each cooler will be checked against information provided on the chain of custody/request for analysis forms. Cooler temperatures and specified sample preservation will also be verified and recorded.	I/E	Martha Maier Vista Analytical Laboratory Julie Ellingson ALS Environmental
Internal laboratory chain of custody records	A complete set of chain of custody records must be produced and submitted with the data package for each SDG .	I	Martha Maier Vista Analytical Laboratory Julie Ellingson ALS Environmental

See the last page of Worksheet #34 for a description of footnotes.

QAPP Worksheet #34
Verification (Step I) Process (Continued)

VERIFICATION INPUT	DESCRIPTION	INTERNAL/ EXTERNAL	RESPONSIBLE FOR VERIFICATION (NAME, ORGANIZATION)
Case Narrative to include the following: • Identification of QC samples • Communication logs • Corrective action reports • Documentation of corrective action results • Documentation of laboratory method deviations • Signatures for laboratory sign-off	Verify completeness and accuracy prior to shipping the laboratory report.	I	Martha Maier Vista Analytical Laboratory Julie Ellingson ALS Environmental
Laboratory data package deliverables as specified in Worksheet #29-2	All laboratory data packages will be verified by the laboratory performing the work for completeness and technical accuracy prior to shipping the laboratory report.	I	Martha Maier Vista Analytical Laboratory Julie Ellingson ALS Environmental
Laboratory electronic data deliverables as specified in Worksheet #29-4	All laboratory electronic data packages will be verified by the laboratory performing the work for completeness and technical accuracy prior to shipping the laboratory report.	I	Martha Maier Vista Analytical Laboratory Julie Ellingson ALS Environmental
Laboratory and field data packages and electronic data deliverables as specified in Worksheets #29-2, #29-3, and #29-4	All received data packages will be verified for completeness according to the data validation procedures specified in Worksheet #s 34, 35, and 36.	E	Diane Waldschmidt Environmental Data Services, LTD.

Notes:

E = External in relation to data generator
FSIWP/QAPP = Focused Sediment Investigation Work Plan/Quality Assurance Project Plan
I = Internal in relation to data generator
QC = quality control
SDG = sample delivery group

QAPP Worksheet #35
Validation (Steps IIa and IIb) Process

Step IIa/IIb	Validation Input	Description of Validation Procedure	Organization Responsible for Validation
IIa	Data deliverables and QAPP	Ensure that all required information on sampling and analysis from data verification was provided.	Environmental Data Services, Ltd.
IIa	Analytes	Ensure that required lists of analytes were reported as specified in this FSIWP/QAPP.	Environmental Data Services, Ltd.
IIa	Chain of custody	Examine the traceability of the data from time of sample collection until reporting of data. Examine chain of custody records against contract, method, or procedural requirements.	Environmental Data Services, Ltd.
IIa	Holding times	Identify holding time criteria and either confirm that they were met or document deviations. Confirm that samples were analyzed within holding times specified in this FSIWP/QAPP. If holding times were not met, confirm that deviations were documented, that appropriate notifications were made (consistent with procedural requirements), and that approval to proceed was received prior to analysis.	Environmental Data Services, Ltd.
IIa	Sample handling	Confirm that required sample handling, receipt, and storage procedures were followed, and that any deviations were documented. Sample preservation and temperature will specifically be evaluated and documented.	Environmental Data Services, Ltd.
IIa	Sampling methods and procedures	Establish that required sampling methods were used and that any deviations were noted. Confirm that the sampling procedures and field measurements met performance criteria and that any deviations were documented.	Environmental Data Services, Ltd.
IIa	Analytical methods and procedures	Establish that required analytical methods were used and that any deviations were noted.	Environmental Data Services, Ltd.
IIa	Data qualifiers	Determine that the laboratory data qualifiers which were defined in Worksheet #29-3, were applied as specified in this FSIWP/QAPP.	Environmental Data Services, Ltd.

See the last page of Worksheet #35 for a description of footnotes.

QAPP Worksheet #35
Validation (Steps IIa and IIb) Process (Continued)

Step IIa/IIb	Validation Input	Description of Validation Procedure	Organization Responsible for Validation
IIa	Laboratory transcription	Confirm accuracy of the transcription of analytical data (i.e., laboratory notebook to reporting form and instrument to laboratory information management system).	Environmental Data Services, Ltd.
IIa	Standards	Determine that standards are traceable and meet contract, method, or procedural requirements.	Environmental Data Services, Ltd.
IIa	Communication	Establish that required communication procedures were followed by field or laboratory personnel.	Environmental Data Services, Ltd.
IIb	Field duplicates	Compare results of field duplicates with criteria established in this FSIWP/QAPP.	Environmental Data Services, Ltd.
IIb	Project quantitation limits	Determine that quantitation limits were achieved, as outlined in this FSIWP/QAPP.	Environmental Data Services, Ltd.
IIb	Confirmatory analyses	Evaluate agreement between results of confirmatory analyses.	Environmental Data Services, Ltd.
IIb	Performance criteria	Evaluate QC data against project-specific performance criteria in this FSIWP/QAPP (i.e., evaluate quality parameters beyond those outlined in the methods).	Environmental Data Services, Ltd.
IIb	Analytical methods and procedures	Evaluate results of required QC samples and compare with acceptance criteria established in this FSIWP/QAPP.	Environmental Data Services, Ltd.
IIb	Data validation reports	Full data validation will be performed on all analytical parameters. Summarize deviations from methods, procedures, or contracts. Summarize outcome of comparison of data to measurement performance criteria in this FSIWP/QAPP. Include qualified data and explanation of all data qualifiers.	Environmental Data Services, Ltd.

Notes:

FSIWP/QAPP = Focused Sediment Investigation Work Plan/Quality Assurance Project Plan
QC = quality control
QL = quantitation limit

QAPP Worksheet #36
Validation (Steps IIa and IIb) Summary

Concentration: Low

ANALYTICAL GROUP	REFERENCE NUMBER	VALIDATION CRITERIA[1]	DATA VALIDATOR
HCX	V-1	EDS SOP, HCX Rev.1, 8/11	Environmental Data Services, Ltd.
PCDDs/PCDFs	V-2	USEPA Region 2 SOP HW-25, Rev. 3	Environmental Data Services, Ltd.
Cs-137	V-3	EDS SOP RAD-1 Rev. 4, 7/07	Environmental Data Services, Ltd.

Notes:

[1] All validation and verification reference documents have been provided as appendices to this FSIWP/QAPP.

Cs-137 = Cesium-137
EDS = Environmental Data Services, Ltd.
HCX = 1,2,4,5,7,8-hexachlor(9H)xanthene
PCDDs/PCDFs = polychlorinated dibenzo-*p*-dioxin/polychlorinated dibenzofurans
SOP = Standard Operating Procedure
USEPA = U.S. Environmental Protection Agency

QAPP Worksheet #37
Usability Assessment

The Data Usability Assessment will be performed by Diane Waldschmidt, Director, Environmental Data Services, Ltd. Note that the Data Usability Assessment will be conducted on validated data. The results of the Data Usability Assessment will be presented in the final project report. The following items will be assessed and conclusions drawn based on their results.

Precision

Results of all laboratory and field duplicates will be evaluated based on the measurement performance criteria presented on Worksheet #12-2. A discussion will follow, summarizing the results of laboratory precision. Any conclusions about the precision of the analyses or sample collection techniques will be drawn and any limitations on the use of the data will be described.

Accuracy/Bias Contamination

Results for all laboratory method blanks and instrument blanks, as well as field rinsate blanks will be evaluated. The results for each analyte will be checked against the measurement performance criteria presented on Worksheets #12-1 and #12-2. A discussion will follow, summarizing the results of laboratory and field accuracy and bias. Any conclusions about the accuracy and bias of the analyses based on contamination will be drawn and any limitations on the use of the data will be described.

Overall Accuracy/Bias

The results for all matrix spike and surrogate standard spike analyses will be evaluated based on the requirements listed in Worksheets #12-1 and #12-2. A discussion will follow, summarizing overall accuracy and bias. Any conclusions about the overall accuracy and bias of the analyses will be drawn and any limitations on the use of the data will be described.

Sensitivity

All analytical results reported will be evaluated to determine if adequate sensitivity was achieved. The results for each analyte will be cross-checked against the quantitation limits presented in Worksheets #15-1 and #15-2. Results for analytes that do not meet project quantitation limits will be summarized. A discussion will follow, detailing the results of the laboratory-sensitivity evaluation. Any conclusions about the sensitivity of the analyses will be drawn and any limitations on the use of the data will be described.

QAPP Worksheet #37
Usability Assessment (Continued)

Representativeness

Representativeness is achieved through adherence to sampling and analytical procedures described in this Focused Sediment Investigation Work Plan/ Quality Assurance Project Plan (FSIWP/QAPP) and compliance with stipulated sample holding times. After evaluation of relative compliance with specified procedures and holding times, conclusions about data representativeness will be drawn and any limitations on the use of data will be described.

Comparability

Data comparability will be assessed through evaluation of achieved sample-specific reporting limits, units of measure, and adherence to specified analytical methodologies and field/sample collection standard operating procedures specified in the FSIWP/QAPP. Evaluation of field procedures used will include assessment of the affects of any deviation from the established filed procedures to data usability. After the evaluations are completed, conclusions about data comparability will be drawn and any limitations on the use of data will be described.

Completeness

A completeness check will be done on all of the data generated. Field and analytical completeness criteria are presented on Worksheets #12-1 and #12-2. Field and analytical completeness will be calculated for each analytical group as follows:

The field completeness will be calculated by the ratio of the number of samples received in acceptable condition by the laboratories to the number of samples planned to be collected as specified in this document. The equation for field completeness is:

$$\%\ Field\ Completeness = \frac{Number\ of\ Samples\ Received\ by\ Laboratories}{Total\ Number\ of\ Samples\ Planned\ to\ be\ Collected}\ x\ 100$$

The analytical completeness will be calculated by the ratio of total valid analytical data results (including estimated values) to the total number of analytical results requested on samples submitted for analysis. Valid analytical data results are defined as those that were not rejected during data validation, due to a significant quality assurance/quality control problem. The equation for analytical completeness is:

$$\%\ Analytical\ Completeness = \frac{Total\ Valid\ Analytical\ Data}{Analytical\ Data\ Obtained}\ x\ 100$$

Figures

Figure 1

Passaic River

2

E 17
E 16
E 15
E 14
E 13
E 12
E 11
E 10
E 9
E 8
E 7
E 6
E 5
3 E
4 E
E 2
E 1

Group B Sample Locations, RM 11.5

Group A Sample Locations, RM 10.9

Group C Sample Locations, RM 7.8

0 0.5 1 2 Miles

RM = River Mile
In-Channel Passaic River Mile Denoted by (E)

ENVIRON

Passaic River

Figure
1

Figure 2

Group A Sample Locations River Mile 10.9

2

A1

A2

A3

Location: A1
River Mile: 10.81
Northing: 723378.10
Easting: 593405.51

Location: A2
River Mile: 10.74
Northing: 723193.04
Easting: 593175.60

Location: A3
River Mile: 10.70
Northing: 723107.84
Easting: 592915.84

0 0.25 0.5 Miles

0 50 100 200 Feet

NAD_1983_StatePlane_New_Jersey_FIPS_2900_Feet
Source: ESRI, i-cubed, USDA FSA, USGS, AEX, GeoEye, Getmapping, Aerogrid, IGP

ENVIRON

Group A Sample Locations River Mile 10.9

Figure 2

Figure 3

Group B Sample Locations River Mile 11.5

2

B1

B2

Location: B1
River Mile: 11.30
Northing: 724482.53
Easting: 595821.83

Location: B2
River Mile: 11.23
Northing: 724299.51
Easting: 595629.74

0 0.25 0.5 Miles

0 50 100 200 Feet

NAD_1983_StatePlane_New_Jersey_FIPS_2900_Feet
Source: ESRI, i-cubed, USDA FSA, USGS, AEX, GeoEye, Getmapping, Aerogrid, IGP

ENVIRON

Group B Sample Locations River Mile 11.5

Figure 3

Figure 4

Group C Sample Locations River Mile 7.8

2

C1

C2

Location: C1
River Mile: 7.71
Northing: 708051.18
Easting: 588849.01

Location: C2
River Mile: 7.64
Northing: 707854.96
Easting: 588760.11

0 0.25 0.5 Miles

0 50 100 200 Feet

NAD_1983_StatePlane_New_Jersey_FIPS_2900_Feet
Source: ESRI, i-cubed, USDA FSA, USGS, AEX, GeoEye, Getmapping, Aerogrid, IGP

ENVIRON

Group C Sample Locations River Mile 7.8

Figure 4

Appendix A

Field Standard Operating Procedures

SOP 1
STANDARD OPERATING PROCEDURES
DECONTAMINATION

1.0 Scope and Application

The purpose of this document is to define the standard operating procedure (SOP) for decontamination of equipment, instruments, and other materials used during implementation of the focused sediment investigation within the Lower Passaic River Study Area (LPRSA) in Bergen, Essex, Hudson, and Passaic Counties, New Jersey. Decontamination is the process of neutralizing, washing, and rinsing exposed surfaces of equipment to minimize the potential for contaminant migration and/or cross-contamination. This procedure does not apply to personnel decontamination.

Other SOPs will be utilized with this procedure, including:

- SOP 6 - Management and Disposal of Residuals;
- SOP 7 - Field Documentation; and
- SOP 8 - Containers, Preservation, Handling, and Tracking of Samples for Analysis.

2.0 Materials

The following list summarizes materials which may be utilized during the implementation of the procedures detailed in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Personal protective equipment (PPE) and other safety equipment;
- Bristle brushes;
- Wash/rinse tubs;
- Low phosphate detergent;
- 10% nitric acid, ultrapure;
- Acetone, methanol, and hexane (pesticide grade or better in separate Teflon bottles), as necessary;
- Deionized "analyte-free" water;
- Stainless steel bowls;
- Aluminum foil;
- Tap water (from any treated municipal water supply);
- High-pressure/steam cleaner;
- Sample container(s) for rinsate blank, if collected; and
- Logbook.

3.0 Procedure

3.1 Sampling Equipment Decontamination

Sampling equipment (including newly purchased equipment) that comes into contact with the media to be sampled will be decontaminated prior to use in the field to eliminate or minimize cross-contamination. The frequency of decontamination is provided in SOP 3 – Sediment Collection Using Hand Coring Device, SOP 4 – Sediment Collection Using Vibracoring Device, and SOP 5 – Core Processing. Sufficient decontaminated equipment must be available to be dedicated to the sampling locations planned for each day. Equipment will be decontaminated in the area designated for decontamination.

The decontamination procedure followed by United States Environmental Protection Agency (USEPA) Region 2 (USEPA, 1989) – with the exception of the second tap water rinse being replaced with a deionized "analyte-free" water rinse – will be used prior to each sampling event for equipment that will come into contact with the environmental media to be sampled. The USEPA Region 2 procedures are summarized below:

1. Wash and scrub with low phosphate detergent.
2. Rinse with tap water.
3. Rinse with 10% nitric acid (HNO3), ultrapure.
4. Rinse with deionized "analyte-free" water.
5. Spray or rinse with acetone only or a methanol followed by hexane spray or rinse (solvents must be pesticide grade or better).
6. Rinse thoroughly with deionized ("analyte-free") water.
7. Air dry.
8. Wrap in aluminum foil, shiny side out, for temporary storage and transport.

Sampling equipment will be decontaminated as described in Sections 3.1.1, 3.1.2, and 3.1.3, below. Solvents used during decontamination activities will be collected and handled in accordance with residuals management procedures outlined in SOP 6 – Management and Disposal of Residuals.

Not all sampling equipment will require the full decontamination procedures listed in the USEPA Region 2 CERCLA Quality Assurance Manual. Three levels of decontamination (i.e., solvent [Section 3.1.1], soap and water [Section 3.1.2], or river water decontamination [Section 3.1.3]) will be performed based on the usage of the sampling equipment as defined below.

3.1.1 Decontamination with Solvents

The following steps will be used to decontaminate small sampling equipment that will come into contact with sediment designated for chemical analysis (e.g., stainless steel trowels, spoons and bowls, polybutyrate core tubes, stainless steel core cutters and catchers, and plastic caps for the core tubes):

1. Personnel will dress in suitable PPE to reduce exposure to chemicals and contaminants.

2. Residual sample media at the coring location will be scraped off and the equipment rinsed with river water, while still on station at the sampling location.

3. Residual sample media on equipment at the sample processing site will be scraped off and collected according to residuals management procedures outlined in SOP 6 – Management and Disposal of Residuals.

4. Equipment will be placed in a wash tub or bucket containing Alconox (or other low-phosphate detergent) along with tap water, and scrubbed with a bristle brush or similar utensil. Equipment will be rinsed with tap water in a second wash tub or bucket, followed by a nitric acid rinse (for metals analyses), a deionized "analyte-free" water rinse, a methanol rinse followed by a hexane rinse (for organic analyses), and lastly with a deionized water rinse. Rinses shall utilize sufficient amounts of solvent/water to flush rather than just wet the

surface. The volume of deionized water used during the rinse must be at least five times the volume of solvent used.

5. Following decontamination, equipment will be placed in a clean area and allowed to air dry. Following air drying, the equipment will be wrapped in aluminum foil, shiny side out, until used for sample collection.

6. Used decontamination water will be collected and handled in accordance with residuals management procedures outlined in SOP 6 – Management and Disposal of Residuals.

3.1.2 Decontamination with Soap and Water

The following steps will be used to decontaminate equipment that is not intended to collect samples for chemical analysis:

1. Personnel will dress in suitable PPE to reduce exposure to contaminants.

2. Residual sample media at the coring location will be scraped off and the equipment rinsed with river water, while still on station at the sampling location.

3. Residual sample media on equipment at the sample processing site will be scraped off and collected according to residuals management procedures outlined in SOP 6 – Management and Disposal of Residuals.

4. Equipment will be placed in a wash tub or bucket containing Alconox (or other low-phosphate detergent) along with tap water, and scrubbed with a bristle brush or similar utensil. Equipment will be rinsed with tap water in a second wash tub or bucket, and then rinsed again.

5. Following decontamination, equipment will be placed in a dedicated clean area.

6. Rinse water and detergent water will be replaced frequently. Used decontamination water will be collected and handled in accordance with residuals management procedures outlined in SOP 6 – Management and Disposal of Residuals.

3.1.3 Decontamination with River Water

The following steps will be used to decontaminate sampling and support vessels, vessel anchors, lines, ropes, submersible pump and hose (not intended for sample collection), vibracoring head, and buoy marker weights:

1. Personnel will dress in suitable PPE to reduce exposure to contaminants.

2. Equipment will be rinsed with river water onboard the sampling vessel.

3. Rinse water will not be contained.

Daily decontamination of the decks of the vessels will consist of river water washing as soon as possible after concluding work. Further wash-down with tap water at the marina is at the discretion of the boat's captain.

3.2 Field Instruments and Equipment

Instrumentation should be cleaned according to the manufacturer's instructions. Care will be taken to prevent damage to equipment. When possible, instruments that are difficult to decontaminate, such as cameras and data logging instruments, may be protectively wrapped to reduce or eliminate the need for decontamination.

3.3 Other Equipment Decontamination

Other sampling equipment that might be used that has had direct contact with sediments or wastes shall be decontaminated at a designated area prior to leaving the site. The decontamination procedure will be as follows:

1. Equipment will be wrapped or draped in plastic or placed in the plastic-lined cargo area of a truck for transport to the area designated for decontamination.

2. Equipment will first be washed with a hot water, high-pressure spray or steam-cleaned.

3. Equipment will then be rinsed, by hose or high pressure spray, with tap water.

4. Wash and rinse water will be collected and handled in accordance with residuals management procedures outlined in SOP 6 – Management and Disposal of Residuals.

3.4 Equipment Leaving LPRSA

Equipment leaving the site upon the completion of focused sediment investigation activities will be decontaminated according to Sections 3.1, 3.2, or 3.3 above.

3.5 Collection of Rinsate Blank

Rinsate blanks will be collected to assess the adequacy of equipment decontamination procedures. Rinsate blanks are submitted for testing each day a decontamination event is carried out (not to exceed one per day). A minimum of two sets of equipment will be available for sampling/processing to accommodate the collection of cores and processing of samples on alternating days. Following sample collection and processing, all pieces of equipment (both used and unused) belonging to the equipment set will be decontaminated during the decontamination event. One set of equipment will be used throughout the sample collection and processing activities to ensure the rinsate blank corresponds to one set of samples.

The rinsate blank collection procedures are as follows:

1. Pour analyte-free water over a representative set of sampling equipment (e.g., core cutter, stainless steel bowl, stainless steel pan) after it has been decontaminated.

2. Collect rinsate in a previously decontaminated stainless steel bowl and transfer rinsate to sample bottles for analysis with other sediment samples.

3. Preserve rinsate sample, as necessary, in accordance with SOP 8 – Containers, Preservatives, Handling, and Tracking of Samples for Analysis.

4.0 Quality Assurance

Decontamination quality assurance (QA) procedures described in Section 3.5 will be performed to assess the adequacy of equipment decontamination procedures. Rinsate blanks will be collected at the frequency specified in the FSIWP QAPP.

5.0 Field Documentation

Field personnel are responsible for documenting decontamination activities related to their onsite activities in accordance with SOP 7 – Field Documentation. As specified in SOP – 7 Field Documentation, a description of the decontamination procedures will be documented in a logbook and include, by date, a list of equipment being decontaminated, a brief description of the procedure and materials used during the process, and the names of the project staff performing the decontamination.

6.0 References

USEPA. 1989. Region II CERCLA Quality Assurance Manual. Revision 1.

ENVIRON. 2011. Focused Sediment Investigation Work Plan – Lower Passaic River Study Area. August.

SOP 2
STANDARD OPERATING PROCEDURES
POSITIONING

1.0 Scope and Application

The purpose of this document is to define the standard operating procedure (SOP) for positioning coring vessels during implementation of focused sediment investigation within the Lower Passaic River Study Area (LPRSA) in Bergen, Essex, Hudson, and Passaic Counties, New Jersey. Sediment sampling activities will be conducted from a coring vessel.

In accordance with the procedures outlined below, these vessels must be properly positioned and their position recorded before each activity can begin. Positioning will be conducted to locate the vessel(s) with sufficient accuracy and precision to meet project objectives during the sediment sampling activities. This SOP describes the equipment, field procedures, materials, and documentation procedures necessary to position coring vessels.

Other SOPs will be utilized with this procedure, including:

- SOP 3 - Sediment Collection Using Hand Coring Device;
- SOP 4 - Sediment Collection Using Vibracoring Device; and
- SOP 7 - Field Documentation.

2.0 Materials

The following list contains materials which may be needed in carrying out the procedures contained in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Personal protective equipment (PPE) and other safety equipment;
- Vessel(s) adequate for LPRSA conditions;
- 25 watt marine VHF radio;
- Navigation charts;
- Differential Global Positioning System (DGPS) that utilizes United States Coast Guard (USCG) differential corrections and having a horizontal accuracy of +/-1 meter;
- DGPS External Antennas (x2);
- Equipment user manuals;
- Table of target sampling location coordinates;
- Assorted nautical equipment (e.g., anchors, lines, personal flotation devices);
- Core Collection Forms, Individual Core Collection Forms, and Grab Sample Collection Forms;
- Permanent marker or grease pencil; and
- Logbook.

3.0 Procedure

This section gives the step-by-step procedures for vessel positioning. A DGPS will be used to establish locations during implementation of activities specified in the FSIWP. Observations made during vessel positioning should be recorded on the Core Collection Form, Individual Core Collection Form, and/or logbook, as appropriate.

While this SOP provides general guidance and procedural steps, personnel performing positioning activities also should follow the appropriate sections of equipment user's manuals and have the manuals available for reference at all times.

The following procedures describe the steps to establish position at a location, as well as the steps to adjust the positioning for collection of additional cores.

3.1 Establishing Position at a Location

3.1.1 Preliminary Activities

1. Obtain the appropriate form(s) (i.e., Core Collection Form, Individual Core Collection Form). Complete the Daily Activity Log provided in SOP 7 - Field Documentation.

2. Obtain the target sampling locations. The location of each target sampling location will be established in the New Jersey State Plane Coordinate System with respect to the North American Datum of 1983 (NAD83).

3. Enter into the vessel's DGPS, as a waypoint, the coordinates for the locations to be occupied.

3.1.2 Field Activities

1. Prior to coring operations, establish a DGPS base station over a shore-based marker with known coordinates and accuracy. The operation and horizontal accuracy of the vessel mounted DGPS will be verified at another shore-based marker with known coordinates by recording observed horizontal data and comparing these data to the published data for that point. After initial DGPS system verification, a temporary benchmark may be established at a location convenient to the vessel to facilitate daily verification of DGPS system performance. Verification of DGPS system performance will be conducted twice per day and documented in the log book and vessel data logger. Horizontal coordinates will be recorded in New Jersey State Plane coordinates with an accuracy of +/- one meter.

2. Verify receiving antenna is properly aligned with the sampling device (e.g., vibracorer).

3. Identify and approach actual sampling locations by using data from the DGPS unit in the navigation mode. The navigation mode provides information on heading, distance remaining, and time remaining. This information is based on the selected waypoint location and the present location of the vessel.

4. Anchor the vessel at the planned location sediment coring sample location,

5. Once the vessel is on location and secured, note the coordinates from the DGPS unit and check the coordinates to verify that the vessel is within the pre-determined range of the target location. For the initial coring attempt, ensure that the coordinates are within 5 feet of the target. (For subsequent coring attempts, see Section 3.2 below.) If not acceptable, adjust the vessel's location, and recheck the position. Repeat this process until the vessel's position is within acceptable range of the target. Record the final coordinates on the appropriate form.

6. Once the coordinates are acceptable, perform activity at the location. For the field activities, collect cores in accordance with the appropriate SOP, either SOP 3 – Sediment Collection Using Hand Coring Device or SOP 4 – Sediment Collection Using Vibracoring Device. Record final location coordinates on the appropriate form once the coring device has penetrated the sediment to the target depth or refusal and prior to retrieval. Plot location onto a master chart or use computer-based, real-time software to verify location.

7. At the end of the sampling day, check the data loaded into the DGPS units to verify the existence of coring locations where data were collected.

3.2 Adjusting Position for Multiple Cores or Coring Attempts at One Location

It is possible that core refusal may be encountered during the focused sediment investigation field activities. In the event core refusal is encountered before the target penetration depth, the field crew will attempt to obtain the targeted penetration depth no more than three times. The following steps will be used to adjust position for multiple cores or coring attempts at one location.

1. Move vessel 10 feet from initial coring/sampling location and within a 50-foot radius of the target coordinates.

2. Check the coordinates to verify that the vessel is within 5 feet of the target coordinate and note coordinates on the Individual Core Collection Form or Grab Sample Collection Form.

3. Once the coordinates are acceptable and recorded, collect cores in accordance with SOP 3 – Sediment Collection Using Hand Coring Device, or SOP 4 – Sediment Collection Using Vibracoring Device. Record the final core location on the Individual Core Collection Form. Plot location onto a master chart or use computer-based, real-time software to verify location.

4. Repeat Steps 1 through 3 until the appropriate number of cores are collected or full number of coring attempts have been exhausted.

4.0 Maintenance

Prior to use, the DGPS units will be inspected and calibrated in accordance with the FSIWP QAPP and appropriate sections of the equipment user's manual. Maintenance and use of DGPS units should follow the appropriate sections of the equipment user's manual. Field personnel will have the manual available for reference. Equipment inspection and maintenance will be recorded in the equipment maintenance log.

Despite virtually worldwide, 24-hour coverage, technical difficulties with GPS satellites can still occur. In the event of system-wide or other long-term problems with GPS (e.g., satellite failures), vessel positioning will be achieved using land-based methods. If a land-based method is selected, an SOP will be developed for its use.

5.0 Quality Assurance

For the focused sediment investigation field activities, quality assurance activities for positioning procedures include verification of the core location by comparing the target coordinates with coordinates entered into the DGPS, and by plotting the coordinates on a master chart.

6.0 Field Documentation

Detailed positioning data will be recorded on the Individual Core Collection Form provided in SOP 7 – Field Documentation. In addition, the following information will be recorded in a logbook (at a minimum):

- Notes on breaking position during coring;
- Equipment calibration information; and
- Summary of vessel activities.

7.0 References

ENVIRON. 2011. Focused Sediment Investigation Work Plan – Lower Passaic River Study Area. August.

SOP 3
STANDARD OPERATING PROCEDURES
SEDIMENT COLLECTION USING HAND CORING DEVICE

1.0 Scope and Application

The purpose of this document is to define the standard operating procedure (SOP) for collecting cores using a hand coring device during implementation of focused sediment investigation within the Lower Passaic River Study Area (LPRSA) in Bergen, Essex, Hudson, and Passaic Counties, New Jersey. This SOP describes the equipment, field procedures, materials, and documentation procedures necessary to collect cores.

Other SOPs will be utilized in conjunction with this SOP, including:

- SOP 1 - Decontamination;
- SOP 2 - Positioning;
- SOP 5 - Core Processing;
- SOP 6 - Management and Disposal of Residuals; and
- SOP 7 - Field Documentation.

2.0 Materials

The following equipment list contains materials which may be needed in carrying out the procedures contained in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Personal protective equipment (PPE) and other safety equipment;
- Navigation charts;
- Sampling vessel adequate for LPRSA conditions;
- Marine VHF radio;
- Positioning equipment;
- Decontaminated polybutyrate coring tube with decontaminated end caps;
- Core driver;
- Decontaminated stainless steel core catcher;
- Hacksaw;
- Decontaminated hacksaw blades;
- Decontaminated drill bits;
- Drill;
- Daily Activity Log, Core Collection Form, and Individual Core Collection Form;
- Assorted nautical equipment (e.g., anchors, lines, personal flotation devices [PFDs]);
- Permanent marker or grease pencil;
- Fathometer with a resolution of 0.1 foot;
- 8-inch diameter lead foot configured with steel cable and 50-foot tape measure;
- Tape measure;
- Submersible pump and hose;
- Core storage rack to hold cores vertical and cold during temporary storage on-board coring vessel;
- Duct tape;
- Camera;

- Decontamination equipment/supplies; and
- Logbook.

3.0 Procedure

This section outlines the step-by-step procedures for collecting cores manually using a hand coring device. Observations made during core collection should be recorded on the Daily Activity Log, Core Collection Form, and Individual Core Collection Form, and in a logbook (SOP 7 - Field Documentation).

3.1 Decontamination of Equipment

Decontamination of the polybutyrate core tubes, caps, and stainless steel core catcher will be performed in accordance with procedures outlined in SOP 1 – Decontamination. The decontamination activities will occur on shore and will be conducted with enough time before vessel departure to allow for the decontamination activities to be completed (including drying of the decontaminated equipment). A sufficient amount of decontaminated equipment will be brought on the coring vessel for the planned coring activities for that day. One primary core and one secondary core (nominal 4-inch diameter) will be collected at each location.

3.2 Locating Coring Position

1. The coring schedule for the day will be established prior to vessel departure. The coring crew will be informed prior to departure of the coring locations. One core (nominal 4-inch diameter) will be collected at each location.

2. The coring vessel will move to a coring location in accordance with SOP 2 – Positioning.

3.3 Collection of Cores

1. Complete Daily Activity Log and Core Collection Form.

2. Don PPE.

3. Activate the submersible pump in preparation of cleaning the coring tube and core driver during retrieval.

4. Obtain water depth (to nearest 0.1 foot) from the fathometer or lead foot and record on the Individual Core Collection Form.

5. Determine minimum length of core tubing needed using the following equation:

   Minimum core length needed (feet) = water depth (feet) + target penetration (feet) + 1 foot + stick-up/core driver (feet)

6. On the coring tube, mark the distance to drive the core (target penetration [feet] + water depth [feet] + 1 foot [i.e., plug]). An additional foot of sediment is collected to obtain a "plug" at the bottom of the core (i.e., to minimize the loss of sediment from the core). If necessary, a core catcher may be used to prevent sediment from escaping.

7. Ideally, the core will be collected without the use of a core catcher. At the start of the focused sediment investigation field activities, two attempts will be made at coring without the use of a core catcher. If sediment cannot be retained in the core tube, then core catchers will be used for the remainder of the program.

8. If a core catcher is required, the core catcher will be attached to the bottom of the core tube prior to lowering the core tube into the water.

9. Gently place hand corer on top of the sediment.

10. Lightly drive the coring tube, with straight, vertical entry, into the sediment with a core driver until the targeted core depth is reached (or refusal), as indicated by the markings.

11. Measure and record the penetration on the Individual Core Collection Form. Record final core location coordinates on the Core Collection and Individual Core Collection Forms.

12. To prevent the loss of sediment from the core tube, either use a vacuum pump affixed to an appropriate fitting or use a one-way valve at the top of the core tube.

13. Allow core to remain in place for 10 minutes.

14. While core is "resting" obtain GPS coordinates of core location; record on Core Collection and Individual Core Collection Forms.

15. Slowly pull the tube from the sediment, twisting it slightly as it is removed (if necessary).

16. Before the bottom of the coring tube breaks the water surface, place a cap over the bottom to prevent the loss of material from the core tube. Place the cap on the core tube by reaching down into the water.

17. Bring core to the vessel's deck, maintaining vertical orientation, and secure the cap in place with duct tape. Clean the core tube and core driver by hosing them down with river water. Remove one-way valve. Care should be taken not to direct water into the open end of the core tube.

18. If using a core catcher, remove the core catcher and secure a cap in place with duct tape.

19. Evaluate whether core penetration and recovery are acceptable using the procedures outlined in Sections 3.4 and 3.5, respectively. [Note: When clay is encountered prior to achieving the target depth, procedures used to determine acceptable core penetration will no longer be applicable. For example, if a clay plug is encountered during the first attempt, no additional attempts shall be made. In cases where coring personnel believe that clay was encountered prior to achieving the target depth, but a clay plug was not recovered in the core, up to 3 attempts may be made at that location to obtain a clay plug.

20. Keeping the core tube upright, use a hacksaw with a decontaminated blade or drill with a decontaminated drill bit to make a cut/hole in the core tube approximately 3 to 4 inches above the sediment to allow excess water to seep from the core tube. Continue to make cuts/holes in the core tube, lowering 1 inch each time until reaching the sediment/water interface. When all excess water has been drained from above the sediment/water interface, cut off excess core tube.

21. Cap the cut end of the tube, secure cap with duct tape, and draw an arrow toward this cap. Label "top" to indicate the top of the core. Label the core with the location ID, date, and time, and record this information on the Individual Core Collection Form.

22. Measure the recovered length of the sediment in the core tube (to the nearest 0.1 foot to the extent possible) and record it on the Individual Core Collection Form. The distance between the top of the sediment in the coring tube and the bottom of the coring tube corresponds to the recovered length. Apparent gaps should be noted on the Individual Core Collection Form and the length and location(s) of the gap(s) noted. The total gap length will be subtracted from the total recovery length.

23. Store the core vertically in a core storage rack (capable of keeping cores cold) while on the vessel until it can be transported to the Sample Processing Area. Cores greater than 6 feet will be segmented on the vessel to allow for storage and transportation. Cut these cores at the location of a planned sample segmentation using a hacksaw with a decontaminated blade and recap the exposed ends. Add appropriate markings to indicate the location and segmentation of each section.

24. After repositioning the vessel in accordance with SOP 2 – Positioning, repeat steps 1 through 23 to collect a secondary core to provide additional sample volume.

3.4 Procedures for Determining Acceptable Core Penetration

1. Calculate penetration percentage using the following equation:

$$\text{Penetration}(\%) = \frac{\text{actual penetration}(\text{feet})}{\text{target penetration}(\text{feet})} \times 100$$

   Actual penetration is the depth advanced into the sediment not including the depth advanced to form a plug.

2. Record penetration percentage on the Individual Core Collection Form.

3. If penetration is >75%, then penetration is acceptable. Proceed to Section 3.5, Procedures for Determining Acceptable Core Recovery.

4. If penetration is <75%, then (a) retain core and (b) record on Individual Core Collection Form if low penetration is due to refusal. Record additional penetration notes in Notes section of the Individual Core Collection Form. Move to a new

coring position, in accordance with SOP 2 – Positioning. Upon three unsuccessful attempts to obtain >75% penetration, contact Lead Consultant Project Manager to determine if additional cores should be attempted. Proceed to Section 3.5, Procedures for Determining Acceptable Core Recovery.

3.5 Procedures for Determining Acceptable Core Recovery

1. Calculate recovery percentage using the following equation:

$$\text{Recovery}\,(\%) = \frac{\text{recovery}\,(\text{feet}) - \text{gaps (feet)}}{\text{actual penetration}\,(\text{feet})} \times 100$$

Actual penetration is the depth advanced into the sediment not including the depth advanced to form a plug.

2. Record recovery percentage on the Individual Core Collection Form.

3. If recovery is >75%, then recovery is acceptable. Continue processing core, then move to a new core position in accordance with SOP 2 – Positioning. Proceed to Step 2 of Section 3.3 for collection of second core. If recovery <75%, proceed with Step 4.

4. If recovery is <75%, then (a) retain core; and (b) move to a new coring location in accordance with FLD-1 – Positioning. Upon three attempts to obtain >75% recovery, contact PM to determine if additional cores should be attempted.

5. Upon collection of acceptable cores, proceed to Section 3.6 of this SOP, Management of Cores.

3.6 Management of Cores

1. Containerize excess sediment on the vessel. The field crew will make reasonable attempts to containerize "gross" sediment produced from coring. Sediment residuals generated from rinsing operations will not be included in such containerization. Dispose of solid material (e.g., core tube, caps, sediment) in accordance with SOP 6 – Management and Disposal of Residuals.

2. Verify that the lengths of the core tubes, water depth, and positioning data have been recorded on the Individual Core Collection Form.

3. Prior to transit to the next coring location or return to the marina, decontaminate the core driver and sampling vessel decking as described in SOP 1 – Decontamination.

4. Proceed to next core location specified for that day and repeat above procedures.

5. Completed Core Collection and Individual Core Collection Forms will be provided to the Sample Processing Area personnel when relinquishing cores for processing.

4.0 Quality Assurance

Completing the Daily Activity Log, Core Collection Form, and the Individual Core Collection Form provided in SOP 7 - Field Documentation, will document that the process is being followed and the pertinent information is being collected and recorded in accordance with the procedures outlined in this SOP. Entries in the forms will be double-checked by the samplers to verify the information is correct. Completed forms will be reviewed periodically by the Field Team Leader and/or Quality Assurance Coordinator or their designees to verify that the requirements are being met.

5.0 Field Documentation

Field notes will be kept during coring activities in accordance with SOP 7 – Field Documentation. In addition to information contained in the Daily Activity Log, Core Collection Form, and Individual Core Collection Form, times of equipment decontamination will be recorded in a logbook.

6.0 References

ENVIRON. 2011. Focused Sediment Investigation Work Plan – Lower Passaic River Study Area. August.

SOP 4
STANDARD OPERATING PROCEDURES USING VIBRACORING DEVICE

1.0 Scope and Application

The purpose of this document is to define the standard operating procedure (SOP) for collecting cores using a vibracoring device during implementation of focused sediment investigation within the Lower Passaic River Study Area (LPRSA) in Bergen, Essex, Hudson, and Passaic Counties, New Jersey. This SOP describes the equipment, field procedures, materials, and documentation procedures necessary to collect cores.

Other SOPs will be utilized in conjunction with this SOP, including:

- SOP 1 - Decontamination;
- SOP 2 - Positioning;
- SOP 5 - Core Processing;
- SOP 6 - Management and Disposal of Residuals; and
- SOP 7 - Field Documentation.

2.0 Materials

The following list contains materials which may be needed in carrying out the procedures outlined in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Personal protective equipment (PPE) and other safety equipment;
- Navigation charts;
- Sampling vessel adequate for LPRSA conditions;
- Marine VHF radio;
- Positioning equipment;
- Vibracore device;
- Deployment equipment (e.g., A-frame, winch, generator);
- Decontaminated polybutyrate core tubes;
- Decontaminated stainless steel core catcher;
- Decontaminated stainless steel core cutter;
- Hacksaw;
- Decontaminated hacksaw blades;
- Decontaminated drill bits;
- Drill;
- Daily Activity Log, Core Collection Form, and Individual Core Collection Form;
- Core storage racks to hold cores vertical and cold during temporary storage on-board coring vessel;
- Assorted nautical equipment (e.g., anchors, lines, personal flotation devices [PFDs]);
- Permanent marker or grease pencil;
- Fathometer with a resolution of 0.1 foot;
- 8-inch diameter lead foot configured with steel cable and 50-foot tape measure;
- Tape measure;
- Submersible pump and hose;

- Duct tape;
- Camera;
- Decontamination equipment/supplies; and
- Logbooks.

3.0 Procedure

This section gives the step-by-step procedures for collecting cores using a vibracore. Observations made during sediment core collection should be recorded in the Daily Activity Log, Core Collection Form, and Individual Core Collection Form, and a logbook (SOP 7 – Field Documentation).

3.1 Decontamination of Equipment

Decontamination of the polybutyrate core tubes, stainless steel core cutter, and stainless steel core catcher assemblies will be performed prior to vessel departure in accordance with procedures outlined in SOP 1 – Decontamination. The decontamination activities will occur on shore and will be conducted with enough time before vessel departure to allow for the decontamination activities to be completed (including drying of decontaminated equipment). Additional decontaminated equipment and expendable supplies will be carried aboard the coring vessel to cover any unforeseen needs.

3.2 Locating Coring Position

1. The coring schedule for the day will be established prior to vessel departure, and sufficient equipment to complete the work will be on board the sampling vessel. The coring crew will be informed prior to departure of the coring locations and the number of cores required at each location. One primary core and one secondary core (nominal 4-inch diameter) will be collected at each location.

2. The Vibracoring vessel will move to a coring location in accordance with SOP 2 – Positioning.

3.3 Collection of Cores

1. Complete Daily Activity Log and Core Collection Form.

2. Don PPE.

3. Activate the submersible pump in preparation for cleaning the vibracore and coring tube, upon retrieval.

4. At the start of the field program, two attempts will be made at coring without the use of a core catcher. If the sediment cannot be retained in the core tube, then core catchers will be used for the remainder of the program.

5. Slowly winch the vibracore into its deployment orientation.

6. Obtain water depth (to nearest 0.1 foot) from the fathometer or lead foot and record on Individual Core Collection Form.

7. Slowly lower the vibracore to the water surface using the winch. "Zero" this point on the winch cable.

8. Slowly lower the vibracore through the water column, stopping when the cable length paid-out matches the water depth reading from the fathometer.

9. Record second "zero" mark on the winch cable.

10. Lower the vibracore into the sediment.

11. Start the vibracore motor once the tube is just below the sediment-water interface. Record the start time on the Individual Core Collection Form. Slowly penetrate the sediment to the target penetration or refusal based on the second "zero" mark on the cable.

12. Lower vibracore approximately 1 foot more to obtain a "plug" at the bottom of the core (i.e., to minimize loss of sediment from core). Record the end time on the Individual Core Collection Form.

13. On completion of the required penetration, or upon vibracore refusal, turn the motor off. Record the vibracore penetration depth on the Individual Core Collection Form.

14. Record the final core location coordinates on the Core Collection and Individual Core Collection Forms.

15. If a core catcher is not being used, keep the core in position for approximately 10 minutes.

16. Slowly raise the vibracore, while maintaining the core in a vertical position as field conditions allow.

17. Before the bottom of the vibracore breaks the water surface, place a cap over the bottom to prevent the loss of material from the vibracore. Place the cap on the end of the vibracore by reaching down into the water.

18. Bring vibracore to sampling vessel deck while maintaining the core in a vertical position. Remove core cutter and core catcher (if necessary), replace with cap, and secure cap with duct tape.

19. Clean the vibracore barrel and coring assembly by hosing down the equipment with river water as described in SOP 1 – Decontamination

20. Remove the core tube from the vibracore barrel and place a cap on bottom of the coring tube, keeping the core tube in an upright position, as field conditions allow.

21. Return the vibracore device to its onboard, deck storage location.

22. Clean the core tube by hosing it down with river water. Care should be taken not to direct water into the open end of the core tube.

23. Evaluate whether core penetration and recovery are acceptable using the procedures outlined in Sections 3.4 and 3.5, respectively. [Note: When clay is encountered prior to achieving the target depth, procedures used to determine acceptable core penetration will no longer be applicable. For example, if a clay plug is encountered during the first attempt, no additional attempts shall be made. In cases where coring personnel believe that clay was encountered prior to achieving the target depth, but a clay plug was not recovered in the core, up to 3 attempts may be made at that location to obtain a clay plug.]

24. Keeping the core tube upright, as field conditions allow, use a hacksaw with a decontaminated blade or drill with a decontaminated drill bit to make a cut/hole in the core tube approximately 3 to 4 inches above the sediment to allow excess water to seep from the core tube. Continue to make cuts/holes in the core tube, lowering 1 inch each time until reaching the sediment/water interface. When all excess water has been drained from above the sediment/water interface, cut off excess core tube.

25. Cap the cut end of the tube, secure cap with duct tape, and draw an arrow toward the cap. Draw an arrow on the coring tube with permanent marker and label "top" to indicate the top of the core. Label the core with the location ID, date, and time, and record this information on the Individual Core Collection Form.

26. Measure the recovered length of the sediment in the core tube (to the nearest 0.1 foot to the extent possible) and record it on the Individual Core Collection Form. The distance between the top of the sediment in the coring tube and the bottom of the coring tube corresponds to the recovered length. Apparent gaps should be noted on the Individual Core Collection Form and the length and location(s) of the gap(s) should be noted. The total gap length will be subtracted from the total recovery length.

27. Store the core vertically in a core storage rack (capable of keeping cores cold) while on the vessel until it can be transported to the sample processing area. Cores greater than 6 feet will be segmented on the vessel to allow for storage and transportation. Cut these cores using a hacksaw with a decontaminated blade and recap the exposed ends. Add appropriate markings to indicate the location and segment of each section.

28. After repositioning the vessel in accordance with SOP 2 – Positioning, repeat steps 1 through 27 to collect a secondary core to provide additional sample volume.

3.4 Procedures for Determining Acceptable Core Penetration

1. Calculate penetration percentage using the following equation:

$$\text{Penetration}(\%) = \frac{\text{actual penetration}(\text{feet})}{\text{target penetration}(\text{feet})} \times 100$$

Actual penetration is the depth advanced into the sediment not including the depth advanced to form a plug.

2. Record penetration percentage on the Individual Core Collection Form. If penetration is ≥75%, then penetration is acceptable. Proceed to Section 3.5, Procedures for Determining Acceptable Core Recovery.

3. If penetration is <75%, then (a) retain core and (b) record on the Individual Core Collection Form if due to refusal. Record additional penetration notes at the Notes section of the Individual Core Collection Form. Move to a new coring position in accordance with SOP 2 – Positioning. Upon three unsuccessful attempts to obtain >75% penetration, contact Project Manager to determine if additional cores should be attempted. Proceed to Section 3.5, Procedures for Determining Acceptable Core Recovery.

3.5 Procedures for Determining Acceptable Core Recovery

1. Calculate recovery percentage by the following equation:

$$\text{Recovery}(\%) = \frac{\text{recovery}(\text{feet}) - \text{gaps (feet)}}{\text{actual penetration}(\text{feet})} \times 100$$

Record recovery percentage on the Individual Core Collection Form.

2. If recovery is ≥75%, then recovery is acceptable. Continue processing core, then move to a new core location in accordance with SOP 2 – Positioning. Proceed to Step 2 of Section 3.3 for collection of second core. If the recovery <75%, proceed to Step 4.

3. If recovery is <75%, then (a) retain core and (b) move to a new coring position in accordance with SOP 2 – Positioning. Upon three unsuccessful attempts to obtain >75% recovery, contact PM to determine if additional cores should be attempted.

4. Upon collection of acceptable core(s), proceed to Section 3.6 of this SOP, Management of Cores.

3.6 Management of Cores

1. Containerize excess sediment on the vessel. The field crew will make reasonable attempts to containerize "gross" sediment material produced from coring. Sediment residuals generated from rinsing operations will not be included in such containerization. Dispose of solid material (e.g., core tube, caps, sediment) in accordance with SOP 6 – Management and Disposal of Residuals.

2. Verify that the water depth and positioning data have been recorded on the Individual Core Collection Form.

3. Prior to transit to the next coring location or return to the marina, decontaminate

the coring equipment and sampling vessel decking as described in SOP 1 – Decontamination.

4. Proceed to next core location specified for that day and repeat above procedures.

5. Completed Core Collection and Individual Core Collection Forms will be provided to the Sample Processing Area personnel when relinquishing cores for processing.

4.0 Quality Assurance

Completing the Daily Activity Log, Core Collection Form, and the Individual Core Collection Form provided in SOP 7 - Field Documentation, will document that the process is being followed and the pertinent information is being collected and recorded in accordance with the procedures outlined in this SOP. Entries in the forms will be double-checked by the samplers to verify the information is correct. Completed forms will be reviewed periodically by the Field Team Leader and/or Quality Assurance Coordinator or their designees to verify that the requirements are being met.

5.0 Field Documentation

Field notes will be kept during coring activities in accordance with SOP 7 - Field Documentation. In addition to information contained in the Daily Activity Log, Core Collection Form, and Individual Core Collection Form, the times of equipment decontamination will be recorded in a logbook.

6.0 References

ENVIRON. 2011. Focused Sediment Investigation Work Plan – Lower Passaic River Study Area. August.

SOP 5
STANDARD OPERATING PROCEDURES
CORE PROCESSING

1.0 Scope and Application

The purpose of this document is to define the standard operating procedure (SOP) for processing of the cores collected during implementation of focused sediment investigation within the Lower Passaic River Study Area (LPRSA) in Bergen, Essex, Hudson, and Passaic Counties, New Jersey. Core processing includes observational and photologging of cores, and the collection of samples chemical and radiochemical analyses.

Other SOPs will be utilized in conjunction with this SOP, including:

- SOP 1 - Decontamination;
- SOP 3 - Sediment Collection Using Hand Coring Device;
- SOP 4 - Sediment Collection Using Vibracoring Device;
- SOP 6 - Management and Disposal of Residuals;
- SOP 7 - Field Documentation; and
- SOP 8 - Containers, Preservation, Handling, and Tracking of Samples for Analysis.

2.0 Materials

The following equipment list contains materials which may be needed in carrying out the procedures contained in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Personal protective equipment (PPE) and other safety equipment;
- Sample processing table;
- Ruler or measuring tape;
- Hacksaw and supply of decontaminated blades;
- Table of target sample location coordinates;
- Electric sheet metal shears or similar;
- Sampling equipment: stainless steel spoons, spatulas, and bowls;
- Sample bottles for chemical and radiochemical analyses;
- Refrigerator, at 4°C;
- Digital camera with flash;
- Stainless steel dividing blades/knives;
- Unified Soil Classification System (USCS) Charts;
- Photoionization detector (PID) (with calibration kit);
- Core storage rack to hold cores vertical and keep cold prior to processing;
- Grease pencil;
- Appropriate waste disposal equipment;
- Scales to weigh sediment cores and samples; and
- Logbook and associated Core Lithology/Description Forms and Sample Processing Forms.

3.0 Procedure

The core processing procedure presented in this SOP is a multi-step process. The exact procedures and steps will depend on whether the core contains high water content sediments

(i.e., material that would slump if the core is placed horizontally). In advance of processing, each core will be visually inspected to determine if it contains high water content sediments, and consequently, whether it can be processed horizontally or vertically. Cores will then be logged and photographed, and samples will be collected and submitted for chemical and radiochemical analyses.

3.1 Decontamination of Equipment

Decontamination of equipment prior to contact with sediment will be performed in a designated decontamination area. The decontamination will be performed in accordance with procedures outlined in SOP-1 – Decontamination. Equipment decontamination will be conducted sufficiently ahead of the processing activities to allow for the implementation of proper procedures (including drying of decontaminated equipment).

3.2 Preliminary Activities Prior to Processing

The following steps will take place prior to core processing but are "transitional" between coring activities and processing, so, these may occur on the day prior to sample processing.

1. Cores will be maintained in a vertical position in a refrigerated core storage rack while in transit from the coring boat to the Sample Processing Area. At the Sample Processing Area, cores will be stored vertically and kept cold (in either a refrigerator or core storage rack) prior to processing. The Sample Processing Area will be within a secure (i.e., locked) location, allowing for limited access.

2. Upon delivery of the core to the processing laboratory, a hard copy of the forms initiated for each core during coring operations, the Daily Activity Log, the Core Collection Form, and the Individual Core Collection Form, will be provided to the Sample Processing Area personnel (SOP 7 - Field Documentation). The Individual Core Collection Form will be signed by the coring personnel and the Sample Processing Area personnel. The Individual Core Collection Form will serve as the chain of custody document from the field to the Sample Processing Area.

These steps will be undertaken prior to core processing.

1. Acquire the necessary sampling equipment (e.g., decontaminated stainless steel processing equipment), containers, and label the sample containers with the appropriate sample labels.

2. Transcribe the pertinent field information from the Individual Core Collection Form to the Core Description Form.

3. Dry the surface of the core tube with clean paper towels and measure the length of sediment in the core tube.

4. Adjust the core segmentation scheme by calculating the percent recovery from the actual penetration and the length of sediment in the core tube. All segment lengths will be modified by this same percentage. For example, a core with 80% percent recovery would result in a planned 1-foot segment being modified to a 0.8-foot segment.

5. Following the segment adjustment described in Step 6, measure the length of sediment in each section of core, and compare to the length of sediment in each section as recorded during core collection. To account for differences in sediment length (if any) due to settling in individual sections of the core, further adjust the core segmentation scheme for each section of core by the percent difference in the length of sediment measured after core collection and prior to core processing.

6. Keeping the core vertical, remove top cap from the core to be processed. Visually inspect the sediment in the biologically active zone (BAZ; 0 to 0.5 feet below the sediment surface) and near-surface sediments to determine if they are high water content sediments. High water content sediments would slump if placed horizontally.

7. If the BAZ and near-surface sediments are comprised of high water content sediments then the core will be processed as described in Section 3.3 below.

8. If the BAZ and near-surface sediments are not comprised of high water content sediments, then the core will be processed as described in Section 3.4 of this SOP.

3.3 Core Processing for High Water Content Sediments

As previously described, if the core contains high water content sediments, then the procedures outlined in this section will be used. The procedures involve keeping the core in a vertical position and then carefully removing the high-water content sediments into a stainless steel bowl for processing. The cores cannot be placed horizontally until sediment of sufficiently low water content is reached, such that the sediment will not slump when placed horizontally on the core processing table. Note that a primary and secondary core (to provide additional sediment for laboratory analyses, as needed) will be collected at each location.

1. With the primary core in the vertical position, mark the outside of the core tube with a grease pencil with the appropriate sample interval (0-6"), beginning at the sediment-water interface.

2. Remove all sediment from the 0-6" interval in a ladling fashion using a stainless steel spoon, avoiding sediment from the smear zone, and without disturbing sediment in deeper segments. Place this sediment in a stainless steel bowl.

3. Screen the sediment in the bowls with a PID and record in the Core Lithology/Description form.

4. Visually describe the sediments in the stainless steel bowls. Using the USCS record the description of the sediment type in the appropriate section of the Core Lithology/Description Form. Provide a description of approximate grain size (silt, clay, fine sand, medium sand, coarse sand, and gravel), the presence of observable biota or organic matter, odor, and color. Note any unusual observations in the appropriate column. Identify changes in lithology (such as soil type or grain-size) within the core. If changes in lithology are observed, then the approximate length of various layers will be noted. Changes in lithology will be separated with a line on the Core Lithology/Description Form.

5. Photograph the sediment in the stainless steel bowls. If foreign objects are present or unusual characteristics are noted, photograph the object or unusual characteristic. Make sure an adequate amount of light is available to photograph the sediment and include a photograph ID label in the photograph.

6. Record a description of each photograph in a logbook. Descriptions will include photo number, date, time (24-hour format), core number, depth interval shown in picture, and photographer's name. Unusual observations will also be recorded.

7. Thoroughly mix (homogenize) the sediment in the center of the stainless steel bowl until color and texture differences are no longer detected. Collect samples for chemical and radiochemical analysis. Identify mass of sediment and compare to minimum analyte sample mass requirements. Should insufficient mass exist, default to the sample hierarchical prioritization.

8. Fill pre-labeled sample jars for remaining chemical and radiochemical analyses in accordance with SOP 8 – Containers, Preservation, Handling, and Tracking of Samples for Analysis. Confirm that the sample identification has been recorded in the Sample Processing Form.

9. If determined necessary by the Sample Processing Area personnel, the individual sample bottles may be weighed to ensure appropriate sample volume for lab analysis.

10. Should insufficient sample mass exist from the primary core to fulfill all chemistry and radiochemical analyses, remove all sediment from the 0 to 6-inch interval of the secondary core, place in a separate, clean stainless steel bowl, and homogenize until color and texture differences are no longer detected.

11. Fill pre-labeled sample jars for remaining chemical and radiochemical analyses, in accordance with SOP 8 – Containers, Preservation, Handling, and Tracking of Samples for Analysis. Confirm that the sample identification has been recorded in the Sample Processing Form.

12. Remaining sediment and core tube lengths will be stored or disposed of in accordance with SOP-6 – Management and Disposal of Residuals.

13. For the next sample interval, visually inspect the core to determine whether the next interval contains high water content sediments. If the core does not contain high water content sediments, then the remaining core segments can be processed as described in Section 3.4 below. If the core does contain high water sediments, repeat the core processing procedures specified above in Section 3.3.

3.4 Core Processing for Non-High Water Content Sediments

As described above, if the core does not contain high water content sediments, then the procedures outlined in this section will be used. Appropriate instructions for each group (radiochemistry and chemistry) are provided within the following steps, as necessary. The procedures involve:

- Laying the core horizontal and splitting it lengthwise;
- Screening the core with a PID;
- Collecting samples for chemical and radiochemical analyses; and
- Logging and photologging the cores.

Detailed procedures are as follows:

1. Transfer the core to the sample processing table.

2. Using the electric sheet metal shears (or other cutting device), make two longitudinal cuts along the core tube; one on each side. Open the tube lengthwise and carefully split the core in half. Decontaminated stainless steel dividing plates may be used to ensure equal sectioning.

3. Screen the core with a PID and record in the Core Lithology/Description Form one reading for every 0.5 foot of core screened.

4. Calculate sample intervals for chemical and radiochemical samples using the Sample Processing Form. Mark the specified sampling interval ranges on the outside of the core tube.

5. Prior to collecting samples, transcribe the pertinent field information from the Individual Core Collection Form to the Sample Processing Form.

6. With the core split open, visually describe the core. Using the USCS, record the description of the soil type in the appropriate section of the Core Lithology/Description Form. Provide a description of approximate grain size (silt, clay, fine sand, medium sand, coarse sand, and gravel), the presence of observable biota or organic matter, odor, and color. Note any unusual observations in the appropriate column. Identify changes in lithology (such as soil type or grain-size) within the core. If changes in lithology are observed, then the approximate length of various layers will be noted. Changes in lithology will be separated with a line on the Core Lithology/Description Form.

7. Photograph the exposed section of the core. Include a ruler or measuring tape for scale, and mark the top and bottom and ends of the core. If foreign objects or gaps are present, or unusual observations are made, photograph the object or subject of the observations. Make sure an adequate amount of light is available to photograph core and include a photograph ID label in the photograph.

8. Record a description of each photograph in a logbook. Descriptions will include photo number, date, time (24-hour format), core number, depth interval shown in picture, and photographer's name. Unusual observations will also be recorded.

9. For each sample interval, collect sediment using a decontaminated stainless steel utensil and place in a decontaminated stainless steel bowl. Sediment samples must be obtained such that material in contact with the liner (the "smear zone") is not collected for laboratory analysis.

10. Determine mass of sediment collected and compare to minimum analyte sample mass requirements. Should insufficient mass exist, default to the sample hierarchical prioritization. Thoroughly mix (homogenize) sediment in the center of the stainless steel bowl until color and texture differences are no longer detected.

11. Fill pre-labeled sample jars for remaining chemical and radiochemical analyses, in accordance with SOP 8 – Containers, Preservation, Handling, and Tracking of Samples for Analysis. Confirm that the sample identification has been recorded in the Sample Processing Form.

12. If determined necessary by the Sample Processing Area personnel, the individual sample bottles may be weighed to ensure appropriate sample volume for lab analysis.

13. Remaining sediment and core tube lengths will be stored or disposed of in accordance with SOP-6 – Management and Disposal of Residuals.

3.5 Collection of Quality Assurance Samples

3.5.1 Field Quality Control (QC) Samples

QC samples will be collected during core sample processing. QC samples will be labeled, maintained, and transported in accordance with SOP 8 – Containers, Preservation, Handling, and Tracking of Samples for Analysis. QC samples will include rinsate blanks and field duplicate samples. The QC samples will be collected at the frequency specified in the FSIWP QAPP.

3.5.2 Field Duplicate Samples

Field duplicate samples will be collected following the same procedures as the collection of samples for chemical, radiochemical and geotechnical analyses. One field duplicate sample will be collected for every 20 field samples (per matrix and per method). The duplicate samples will be labeled, maintained, and transported in accordance with SOP 8 – Containers, Preservation, Handling, and Tracking of Samples for Analysis.

3.5.3 Laboratory Quality Control Samples

Matrix spike/matrix spike duplicates (MS/MSD) are required as laboratory QC tests for organic analyses. A laboratory duplicate (laboratory DUP) is required for Cesium-137 analyses. Within each Sample Delivery Group (SDG), one MS/MSD (for organic analysis) and one laboratory DUP (^{137}Cs analyses) must be generated and analyzed by the laboratory for each analytical group submitted. Therefore, field personnel will designate, for each SDG, a sediment sample for each analytical method to be used by the laboratory for these analyses.

4.0 Quality Assurance

Completing the Core Lithology/Description Form and Sample Processing Form provided in SOP 7 - Field Documentation, will document that the process is being followed and pertinent information is being collected and recorded in accordance with the procedures outlined in this SOP. Entries in the forms and logbook will be double-checked by the samplers to verify the information is correct. Completed forms will be reviewed periodically by the Field Team Leader and/or Quality Assurance Coordinator or their designees to verify that the requirements are being met.

5.0 Field Documentation

Field notes will be kept during core processing activities in accordance with SOP 7 – Field Documentation. The core weights and sample weights (if collected) will be recorded in the logbook. In addition, the following core photologging information should also be included in the logbook (at a minimum):

- Photograph number;
- Time of photograph;
- Core number;
- Depth interval shown in the picture;
- Photographer's name; and
- Unusual observations.

6.0 References

ENVIRON. 2011. Focused Sediment Investigation Work Plan – Passaic River Study Area. August.

SOP 6
STANDARD OPERATING PROCEDURES
MANAGEMENT AND DISPOSAL OF RESIDUALS

1.0 Scope and Application

The purpose of this document is to define the standard operating procedure (SOP) for disposal of sediment, water, personal protective equipment (PPE), and other potentially contaminated materials generated during implementation of focused sediment investigation within the Lower Passaic River Study Area (LPRSA) in Bergen, Essex, Hudson, and Passaic Counties, New Jersey. This SOP provides procedures for handling potentially contaminated sediment, water, Personal Protective Equipment (PPE), and other materials during coring and sampling activities through their ultimate disposal.

Other SOPs will be utilized in conjunction with this SOP, including:

- SOP 1 – Decontamination;
- SOP 3 – Sediment Collection Using Hand Coring Device;
- SOP 4 – Sediment Collection Using Vibracoring Device;
- SOP 5 – Core Processing; and
- SOP 7 – Field Documentation.

2.0 Materials

The following equipment list contains materials which may be needed in carrying out the procedures contained in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- PPE or other safety equipment;
- 55-gallon open-top drums (Department of Transportation [DOT] approved) with lid;
- 30-gallon (minimum) garbage bags;
- Permanent marking pens and/or paint pens;
- Labels;
- Duct tape;
- Chemical storage cabinet (meeting Occupational Safety and Health Administration [OSHA] and National Fire Protection Association [NFPA] Code 30 specifications/Factory Manual [FM] approved);
- Indelible ink pens; and
- Logbook.

3.0 Procedure

3.1.1 Solids Residuals for Disposal

Solids residuals generated during field activities will be characterized for appropriate off-site disposal. Solids residuals consist of two types of materials: non-sediment solids materials generated during the collection and processing of cores, including items such as used polybutyrate core tubes, aluminum foil from clean core tubes, PPE (e.g., gloves, Tyvek® suits, boot covers), and sediment not used for analyses (e.g., waste sediment such as that collected from the core "smear zone" and residual sediment). Non-sediment and sediment wastes will be segregated and temporarily stored in separate containers pending disposal. Loose sediment will be removed from non-sediment waste items prior to disposal and stored with other sediment wastes.

If recovered sediment is determined to be unusable after a core has been cut open, the sediment will be removed from the core tube and stored in an appropriate container for disposal as waste sediment. The used core tube will be stored and disposed of with the non-sediment solids wastes. Sediment residuals will be placed in 55-gallon drums, labeled, and stored temporarily until disposal.

Non-sediment solids will be placed in 55-gallon drums, bulk bags and/or a roll-off container, and stored temporarily pending characterization and off-site disposal. All drums and bags containing solids residuals will be labeled and handled as described in Section 3.4 of this SOP.

3.2 Liquid Waste

There are two types of liquid wastes that will be generated: water and chemical. Each will be managed separately.

3.2.1 Waste Water

Waste water will be generated during sediment core processing and decontamination activities. Water from gross decontamination (e.g., to wash sediment from core tubes) will be allowed to flow overboard on the coring vessel or will be decanted and treated at the Lister Avenue groundwater treatment plant. Sediment recovered during this process will be handled according to Section 3.1.1 of this SOP. Water mixed with detergent or chemicals will be treated at the Lister Avenue groundwater treatment plant.

In the event that waste water is not treated through the Lister Avenue groundwater treatment plant, it will be stored at the Lister Avenue Site in appropriate containers pending characterization for off-site disposal.

3.2.2 Chemical Wastes

Spent solvents, acids, and other residual chemicals generated during the decontamination process (SOP 1 – Decontamination) will be collected and treated through the Lister Avenue groundwater treatment plant. In the event that these liquids are not treated through the Lister Avenue groundwater treatment plant, they will be stored at the Lister Avenue Site in appropriate containers pending characterization for off-site disposal.

3.3 Handling and Tracking of Solids Materials and Containers

As they are generated during field activities, waste sediment and other solids waste materials will be placed in DOT-approved 55-gallon drums or 30-gallon bags. Solids which are initially placed in bags may be bulked into 55-gallon drums for storage. The following procedures will be followed for storing sediment and other solids wastes in these drums:

- A drum number will be assigned to each drum by the Field Team Leader or designee. The drum number will be clearly marked on multiple places on the drum;
- A log will be kept for each drum, listing the materials placed in that drum. All solids materials will be segregated based on the type of material (e.g., sediment, coring tubes, PPE, waste plastic, paper, or foil) and, to the extent practicable, by where they were generated (e.g., location within PRSA, etc.);
- Drums will be closed or covered at the end of the day's work;

- Drums containing solids materials will be stored in a secured, temporary facility until proper offsite disposal can be coordinated; and

- Collection drums may be reused at the processing facility after emptying.

3.4 Handling and Tracking of Waste Water and Chemical Wastes and Containers

As they are generated during field activities, waste water and chemical wastes will be treated directly through the on-site Lister Avenue groundwater treatment plant and/or will be placed in separate DOT-approved 55-gallon drums.

The following procedures will be followed for treating the liquids through the on-site groundwater treatment plant:

- A sump will be isolated in the processing area to collect and handle liquids;

- Liquids collected in the sump will be combined and treated with the liquids treated at the on-site groundwater treatment plant; and

- Treated liquids will be monitored, characterized, and disposed of in accordance with the requirements for the on-site groundwater treatment plant.

The following procedures will be followed for storing waste water and chemical liquid wastes in drums:

- A separate drum will be used for each non-commingled chemical. Another, separate drum will be used for chemicals and/or water that have been mixed;

- A drum number will be assigned to each drum by the Field Team Leader or designee. The drum number will be clearly marked on multiple places on the drum;

- A log will be kept for each drum, listing the materials placed in that drum;

- All drums will be closed or covered at the end of the day's work;

- Drums containing waste water and chemical liquid wastes will be stored in a secured temporary facility until proper off-site disposal can be coordinated upon the completion of the sampling event; and

- Collection drums may be reused at the Sample Processing Area after emptying.

3.5 Samples Returned from Off-site Laboratories

Upon completion of the required chemical and/or radiochemical analyses, remaining sample material and sample containers from the laboratory will be returned to the Sample Processing Area. Returned sample material/containers will be transported under chain of custody procedures, and remain in custody until disposal. Upon receipt, the chain of custody form will be signed and the samples will be logged in by a project staff member. The approximate volume of sample material and the condition of the containers in which the samples are returned will be checked and recorded in a logbook.

Samples and empty sample containers will be separated into groups according to sample matrix: sediment, aqueous, sediment containers (empty), and aqueous containers (empty).

Sediment samples will be placed in a DOT-approved 55-gallon drum and will be characterized and disposed of off-site. Empty sediment containers will be properly disposed of by the selected waste disposal subcontractor.

Aqueous samples returned from the analytical laboratories will be treated through the Lister Avenue groundwater treatment plant. In the event that these liquids are not treated through the Lister Avenue groundwater treatment plant, they will be stored at the Lister Avenue Site in appropriate containers pending characterization for off-site disposal.

4.0 Quality Assurance

Disposal actions will be documented in a logbook to ensure that disposal activities are conducted in accordance with the procedures outlined in the SOPs. Waste manifests will be obtained for solids and aqueous waste disposal to verify that proper transportation and disposal of these materials has occurred.

5.0 Field Documentation

The Field Team Leader or designee is responsible for documenting the handling and/or disposal of containers filled with solids or liquids generated during the sediment investigation activities in accordance with SOP 7 - Field Documentation. In addition, the following information should be included in the logbook (at a minimum):

- Name of person performing residual management or disposal activities;
- Date and time of activity;
- Information coordinating container numbers for drums or bags containing solids materials with sample numbers, core boring numbers, or origin; and
- Information coordinating origin of waste liquid (water or chemical[s]) with specific waste drum or tank.

6.0 References

ENVIRON. 2011. Focused Sediment Investigation Work Plan – Lower Passaic River Study Area. August.

SOP 7
STANDARD OPERATING PROCEDURES
FIELD DOCUMENTATION

1.0 Purpose and Scope

The purpose of this document is to define the standard operating procedure (SOP) for documentation of field activities during implementation of focused sediment investigation within the Lower Passaic River Study Area (LPRSA) in Bergen, Essex, Hudson, and Passaic Counties, New Jersey. Appropriate documentation of field activities provides an accurate and comprehensive record of the work performed, sufficient for a technical peer to reconstruct the day's activities and determine that necessary requirements were met.

Other SOPs will be utilized in conjunction with this procedure, including:

- SOP 1 – Decontamination;
- SOP 2 – Positioning;
- SOP 3 – Sediment Collection Using Hand Coring Device;
- SOP 4 – Sediment Collection Using Vibracoring Device;
- SOP 5 – Core Processing;
- SOP 6 – Management and Disposal of Residuals; and
- SOP 8 – Containers, Preservation, Handling, and Tracking of Samples for Analysis.

2.0 Procedures

2.1 General Requirements

Pertinent field information will be recorded in a logbook and/or an appropriate form (as described herein and included in this SOP) in black, ballpoint pen. The field forms may be replaced with a personal data assistant (PDA) and/or an electronic field database. Every form in this SOP includes a key that describes each required entry. Logbook entries will be factual and observational (i.e., no speculation or opinion), and will not contain any personal information or non-project-related entries. Separate and dedicated logbooks will be kept for different operations running concurrently (e.g., core collection onboard the vessel, core processing at the Sample Processing Area); individual tasks making up each operation will be maintained in the same logbook, if possible. The cover and binding of each logbook will be labeled to identify the operation and dates included within the logbook; each page in the logbook will be consecutively numbered.

A page header will appear on the first page of each day's notes in the logbook, and activities for each day will be recorded on a new page. The page header will include:

- name of author and other personnel onsite (and affiliated organization if applicable);
- date;
- time of arrival; and
- current weather and tidal conditions, and weather forecast for the day.

An abbreviated header, limited to the date, will appear at the top of each additional page for the active date. Field forms will require similar header information.

Field activities and other events pertinent to the field activities will be documented in chronological order. Times will be recorded using 24-hour notation for each entry. At a

minimum, documentation in a logbook will include the following:

- name(s) of visitor(s) to the work location being documented in the log, including time of arrival and departure, the visitor's affiliation, and reason for visit;
- summary of project-related communications, including names of people involved and time;
- time daily work commences and ceases;
- start and stop times of new tasks;
- start and stop times of breaks;
- safety or other monitoring data, including units with each measurement;
- deviations from scope of work;
- progress updates;
- problems/delays encountered;
- unusual events; and
- signature or initials of author on every page.

A single line will be drawn through incorrect entries and the corrected entry written next to the original strikeout. Strikeouts are to be initialed and dated by the originator.

If there are additional lines on the page at the end of the day's activities, a line will be drawn through the empty space, initialed, and dated, leaving no room for additional entries.

The logbook will cross-reference information documented in the field forms.

Photographs will be identified in the logbook by a unique numbering system. If photographs are collected by a digital camera, the file number as well as the photograph number will accompany the description of the photograph in the logbook. At a minimum, the time the photograph was taken, the general location, a brief description, and the photographer's name will be recorded. Additional information may include: Differential Global Positioning System (DGPS) coordinates, direction the photographer was facing, and/or weather conditions. If necessary, an object will be included to indicate the scale of the object in the photograph.

2.2 Additional Requirements for Field Activities

This section presents specific documentation requirements for activities to be performed. It is meant to provide guidance to project staff responsible for field documentation during these activities, and is not intended to be a comprehensive list of activities performed. These documentation procedures are meant to supplement, not replace, the required documentation presented in Section 2.1.

As briefly described in Section 2.1, five field forms were developed for the focused sediment investigation to ensure proper documentation of field information is obtained in a consistent manner. The purpose of each form is described below.

- Daily Activity Log – Provides a summary of daily vessel logistics during the focused sediment investigation field activities, including personnel present, equipment used, and weather conditions.

- Core Collection Form – Provides a summary of cores attempted and collected during

each field day.

- Individual Core Collection Form – Provides core-specific information such as penetration and recovery measured during core collection. The Individual Core Collection Form also serves as the chain of custody for the core as it is transported from the coring vessel to the Sample Processing Area.

- Core Lithology/Description Form – Provides a lithological description of a core observed during sample processing.

- Sample Processing Form – Provides core-specific information on sample segmentation.

2.2.1 Equipment Decontamination

Documentation of decontamination procedures will be contained in a logbook and include, by date, a list of equipment being decontaminated, a brief description of the procedure and materials used during the process, and the names of the project staff performing the decontamination. Documentation of QA samples (e.g., rinsate blanks), when collected, will include the information presented in SOP 1 - Decontamination.

2.2.2 Equipment Calibration and Maintenance

Equipment calibration will be recorded, including date of calibration, the instrument manufacturer, model number, and serial number. Instrument calibration will be performed in accordance with manufacturer's specifications. Values measured during calibration and any maintenance/problems/repairs will be recorded.

2.2.3 Vessel Positioning

Information regarding vessel positioning will be recorded in the Daily Activity Logs, the Core Collection Forms, and the Individual Core Collection Forms, all of which are attached to this SOP.

2.2.4 Core Collection

Documentation of core collection will be recorded in the Daily Activity Logs, the Core Collection Forms, and the Individual Core Collection Forms, all of which are attached to this SOP.

2.2.5 Core Processing

Documentation of core processing will be recorded in the Core Lithology/Description Form and Sample Processing Form, both of which are attached to this SOP. Additional information that should be considered for entry into the logbook includes:

- date and time (core processing and individual sample collection);
- names of the members of the processing crew;
- location ID;
- preservative (if necessary);
- processing procedures and equipment; and
- QA samples (matrix spike/matrix spike duplicate [MS/MSD]).

Sample information should be included in a logbook, as well as on the chain of custody form and sample container label.

2.2.6 Sample Handling and Shipping Procedures

Activities associated with the handling and shipping of samples will be recorded in a logbook. In addition to meeting the general requirements presented in Section 2.1, sample handling and shipping documentation will include:

- date and time sample custody was relinquished;
- organization/representative receiving custody;
- name of analytical laboratory;
- tracking number (if using commercial shipping company); and
- Sample Delivery Group (SDG) Tracking Log number (see SOP 8 – Containers, Preservation, Handling and Tracking of Samples for Analysis).

2.3 Distribution and Maintenance of Field Documentation

Logbooks that are taken offsite from the field offices will be photocopied and filed at the end of each day to mitigate against the loss of historical entries should the logbook be lost in the field.

Field data forms and chain of custody forms will be filed once they have been completed and distributed (if necessary), or at the end of each field day.

Distribution of daily forms will be performed according to the needs of the project team and at the direction of the Field Team Leader or designee.

Upon completion of sampling and transfer of samples to the shipping company or courier, copies of the signed chains of custody will be faxed to the Project Manager, appropriate analytical laboratory contact, and the data validator. Copies of these documents will also be maintained at the field office in a labeled three-ring binder in reverse chronological order.

3.0 Quality Assurance

Entries in the field forms (i.e., Daily Activity Log, Core Collection Form, Individual Core Collection Form, Core Lithology/Description Form, and Sample Processing Form) will be double-checked by the samplers to verify the information is correct. Completed field forms will be reviewed periodically by the Field Team Leader and/or Quality Assurance Coordinator or their designees to verify that the requirements are being met.

4.0 References

ENVIRON. 2011. Focused Sediment Investigation Work Plan – Lower Passaic River Study Area. August.

DAILY ACTIVITY LOG
FOCUSED SEDIMENT INVESTIGATION
(Sheet 1 of 2)

I.	Date: (1)			
II.	Vessel Name: (2)			
III.	Personnel (Name/Affiliation/Role): (3)			
IV.	Equipment on Board:	Name/Type	Model No.	Serial No.
	Coring Device:	(4)	(5)	(6)
	DGPS:			
	Fathometer:			
	Other:			
	Other:			
V.	Weather Forecast Checked?: Yes No (7) Description:			
VI.	Time of High and Low Tide Checked? Yes No (8) Description:			

DAILY ACTIVITY LOG
FOCUSED SEDIMENT INVESTIGATION
(Sheet 2 of 2)

I.	Date: (1)
VII.	Health and Safety Briefing Topic: (9)
VIII.	Notification:

Agency	Contact	Time (24-hour)
(10)	(11)	(12)
Vessel Tracking Service		

IX.	Time of Departure from Marina: (13) (24-hour)
X.	Time of Return to Marina: (14) (24-hour)
XI.	Name of Person Responsible for Log: (15)

DAILY ACTIVITY LOG KEY
FOCUSED SEDIMENT INVESTIGATION
(Sheet 1 of 1)

DESCRIPTION OF ITEMS:

(1) Date of activity (e.g., 1/1/2011).

(2) Name of vessel performing activity.

(3) Personnel on vessel, including name, affiliation, and role on the vessel.

(4) Name or type of equipment (e.g., for DGPS, enter Trimble); if specific equipment type not listed, enter under "Other."

(5) Model number of equipment (e.g., for DGPS, enter 7400).

(6) Serial number of equipment (if available).

(7) Weather forecast checked via marine radio, Newark Liberty International Airport, etc.

(8) Time of High and Low Tide for the day checked via NOAA/National Ocean Service's website.

(9) Significant topic(s) discussed at daily health and safety briefing.

(10) Name of Agency(ies) notified of daily activities.

(11) Agency(ies) contact name(s).

(12) Time that Agency(ies) was(were) contacted (24-hour format).

(13) Time of departure from the marina at the beginning of the day (24-hour format).

(14) Time of return to the marina at the end of the day (24-hour format).

(15) Name of person entering information into this form.

CORE COLLECTION FORM
FOCUSED SEDIMENT INVESTIGATION
(Sheet 1 of 2)

I.	Date: _____(1)_____ Start Time: _____(2)_____ End Time: _____(3)_____
II.	Location ID: _____(4)_____
III.	Weather at Time of Coring: - Wind Speed/Direction: _____(5)_____ - Temperature: _____(6)_____ - Precipitation: _____(7)_____ - Cloud Cover: _____(8)_____ - Sea State: _____(9)_____
IV.	Confirm ice in core storage container? Yes No (10)

CORE COLLECTION FORM
FOCUSED SEDIMENT INVESTIGATION
(Sheet 2 of 2)

I.

Date: (1) Start Time: (2)
End Time: (3)

II.

Location ID: (4)

V. Cores Collected: (11)

Core ID (12)	Northing (ft) (13)	Easting (ft) (14)	Disposition (15)

VI.

Name of Person Responsible for Log: (16)

CORE COLLECTION FORM KEY
FOCUSED SEDIMENT INVESTIGATION
(Sheet 1 of 1)

DESCRIPTION OF ITEMS:

(1) Date of coring (e.g., 1/1/2011).

(2) Start time of activities at location (24-hour format).

(3) End time of activities at location in (24-hour format).

(4) Location ID;

(5) Wind speed and direction at time of core collection (e.g., 10-15 mph from NW).

(6) Air temperature at time of core collection (e.g., 68ºF).

(7) Precipitation at time of core collection (e.g., light rain).

(8) Cloud cover at time of core collection (e.g., partly cloudy).

(9) Sea state at time of core collection (e.g., 0-1 foot waves).

(10) Confirm sufficient ice is within core storage container.

(11) Summary of cores collected at location.

(12) Core ID;

(13) Actual Northing coordinate of core collection location in feet.

(14) Actual Easting coordinate of core collection location in feet.

(15) Disposition (e.g., Successful – use for samples; Refusal – retain and discard; Lost sediment upon retrieval, etc.)

(16) Name of person entering information into this form.

INDIVIDUAL CORE COLLECTION FORM
FOCUSED SEDIMENT INVESTIGATION
(Sheet 1 of 4)

I.	Date: (1)
II.	Core ID: (2)
III.	Sediment Collection Method (circle one): (3) - Vibracoring - Hand Coring
IV.	Coordinates: Target Coordinates (New Jersey State Plane NAD 83) - Northing (ft): (4) - Easting (ft): (5) Actual Positioning Coordinates (New Jersey State Plane NAD 83) - Northing (ft): (6) - Easting (ft): (7) For initial coring attempt, confirm final core location coordinates are within 5 feet of target coordinates. For any subsequent attempts, confirm that coordinates are within 10 feet of previous attempt. (8) Actual Core Location Coordinates (New Jersey State Plane NAD 83) - Northing (ft): (9) - Easting (ft): (10) Confirm actual core location coordinates are within 5 feet of target coordinates (11)

INDIVIDUAL CORE COLLECTION FORM
FOCUSED SEDIMENT INVESTIGATION
(Sheet 2 of 4)

I.	Date: _____(1)_____
II.	Core ID: _____(2)_____
V.	Water Depth at Time of Coring (ft): _____(12)_____
VI.	Start Time of Coring (24-hour): _____(13)_____ End Time of Coring (24-hour): _____(14)_____
VII.	Penetration: - Target Penetration (ft): (15) - Actual Penetration (ft): (16) - Penetration (%): _____(17)_____ $\text{Penetration (\%)} = \frac{\text{Actual Penetration (feet)}}{\text{Target Penetration (feet)}} \times 100$ If Penetration (%) ≥ 75%, then penetration is acceptable. If Penetration (%) < 75%, then refer to either SOP No. 3, Section 3.4, or SOP No. 4, Section 3.4 depending on coring method. Refusal? (circle one): Yes No (18)
VIII.	PID Reading: _____(19)_____

INDIVIDUAL CORE COLLECTION FORM
FOCUSED SEDIMENT INVESTIGATION
(Sheet 3 of 4)

I.	Date: _____(1)_____
II.	Core ID: _____(2)_____
IX.	Recovery: - Recovery (ft): _____(20)_____ - Recovery (%): _____(21)_____ Recovery (%) = $\frac{\text{Recovery (ft) - Gaps (ft)}}{\text{Actual Penetration (ft)}}$ x 100 - Gaps Identified _____(22)_____ _____ _____ _____ If Recovery (%) ≥ 75%, then recovery is acceptable. If Recovery (%) < 75%, then refer to either SOP-3, Section 3.5, or SOP-4, Section 3.5, depending on coring method.
X.	Final Disposition of Core (circle one): (23) - Retained for Processing - Rejected If rejected, reason for rejection: _____(24)_____ _____ _____

INDIVIDUAL CORE COLLECTION FORM
FOCUSED SEDIMENT INVESTIGATION
(Sheet 4 of 4)

I.	Date: (1)
II.	Core ID: (2)
XI.	Notes (see logbook for additional information): (25)
XII.	Name of Person Responsible for Log: (26)

Relinquished By (27) Company (28) Date (29) Time (30)

Accepted By (31) Company (32) Date (33) Time (34)

Relinquished By _____ Company _____ Date _____ Time _____

Accepted By _____ Company _____ Date _____ Time _____

INDIVIDUAL CORE COLLECTION FORM KEY
FOCUSED SEDIMENT INVESTIGATION
(Sheet 1 of 2)

DESCRIPTION OF ITEMS:

(1) Date of coring (e.g., 1/1/2011).

(2) Core ID.

(3) Sediment collection method used (e.g., vibracoring or hand coring).

(4) Target Northing coordinate in feet.

(5) Target Easting coordinate in feet.

(6) Actual Position Northing coordinate in feet.

(7) Actual Position Easting coordinate in feet.

(8) Confirm the final position location for the initial coring attempt is within 5 feet of the target location; refer to SOP-2, Section 3.0. Any subsequent attempts are to be within 10 feet of the previous attempt; all within a 50 foot radius of the target coordinates.

(9) Actual Northing coordinate of core collection location in feet. This location may be different than (5) due to the adjustment of vessel position for multiple core attempts at the same location (refer to SOP-2, Section 3.2).

(10) Actual Easting coordinate of core collection location in feet. This location may be different than (6) due to the adjustment of vessel position for multiple core attempts at the same location (refer to SOP-2, Section 3.2).

(11) Confirm the final location is within 50 feet of the target location; refer to SOP-2, Section 3.0.

(12) Water depth at core collection location in feet (to 0.1 ft).

(13) Time core collection with vibracoring or hand coring device is started (24-hour format).

(14) Time core collection with vibracoring or hand coring device is finished in (24-hour format).

(15) Target penetration in feet with vibracoring or hand coring device.

(16) Actual penetration of core into sediment. Actual penetration is the depth advanced into the sediment not including the depth advanced to form a sediment "plug."

Actual penetration (ft) = Penetration (ft) – "plug" (ft)

INDIVIDUAL CORE COLLECTION FORM KEY
FOCUSED SEDIMENT INVESTIGATION
(Sheet 2 of 2)

(17) Penetration (%) - calculated according to formula on form.

(18) If penetration is < 75%, indicate if refusal was encountered.

(19) PID reading in the breathing zone upon screening core.

(20) Recovery (ft) = sediment length in core. To identify gaps, visually inspect the core for signs of separation of the sediments within the core, smears on the polybutyrate core tube walls or a water layer within the sediments. Measure the distance between the top and bottom of these interfaces to obtain the length(s) of the gap(s).

(21) Recovery (%) = sediment length in core per actual penetration.

(22) Record any gaps identified. Record approximate location (feet below the sediment surface) and the size of the gap (feet). For example, "0.1 foot gap observed at 1.5 feet below sediment surface."

(23) Final disposition of core (e.g., retained for processing or rejected).

(24) Provide explanation for rejecting core (e.g., recovery < 75%).

(25) Provide notes pertinent to core collection (e.g., aborted core collection due to weather); additional details may be provided in logbook.

(26) Name of person entering information into this form.

(27) Name of personnel relinquishing core.

(28) Company affiliation of personnel relinquishing core.

(29) Date core is relinquished.

(30) Time core is relinquished (24-hour format).

(31) Name of personnel accepting core.

(32) Company affiliation of personnel accepting core.

(33) Date core is accepted.

(34) Time core is accepted (24-hour format).

CORE LITHOLOGY/DESCRIPTION FORM
FOCUSED SEDIMENT INVESTIGATION
(Sheet 1 of 2)

I.	Date of Core Collection: _____(1)_____(from Individual Core Collection Form)
II.	Date of Core Processing: _____(2)_____
III.	Core ID: _____(3)_____(from Individual Core Collection Form)
IV.	Coordinates: Coordinate Northing (ft, NAD 83): _____(4)_____(from Individual Core Collection Form) Coordinate Easting (ft, NAD 83): _____(5)_____(from Individual Core Collection Form)
V.	Name of Person Responsible for Log: __(6)_____

CORE LITHOLOGY/DESCRIPTION FORM
FOCUSED SEDIMENT INVESTIGATION
(Sheet 2 of 2)

Date of Core Collection: _____(1)_____ Date of Core Processing:____(2)_____

Core ID: _____(3)_____

Depth (Feet Below Sediment Surface in Core)	PID Screening (ppm)	Description	Engineer's/Geologist's Notes
(7)	(8)	(9)	(10)
-1 - -2 - -3 - -4 - -5 - -6 - -7 - -8 - -9 - -10 - -11 - -12 - -13			

CORE LITHOLOGY/DESCRIPTION FORM KEY
FOCUSED SEDIMENT INVESTIGATION
(Sheet 1 of 1)

DESCRIPTION OF ITEMS:

(1) Date of core collection (taken from the Individual Core Collection Form).

(2) Date of core processing (e.g., 1/1/2011).

(3) Core ID.

(4) Northing coordinate in feet of core collection location (taken from the Individual Core Collection Form).

(5) Easting coordinate in feet of core collection location (taken from the Individual Core Collection Form).

(6) Name of person entering information into this form.

(7) Depth (feet below the sediment surface) of change in lithology and Unified Soil Classification System (USCS) description identified during logging. The procedures on how to describe the sediment core are provided in SOP-5.

(8) PID reading in ppm for the breathing zone above the interval screened (e.g., 6 ppm).

(9) Description of soil type using the USCS charts. The procedure of how to describe the sediment core is provided in SOP-5.

(10) Provide notes pertinent to the sample description (e.g., 1" gap observed in this interval) for a given lithological interval.

SAMPLE PROCESSING FORM
FOCUSED SEDIMENT INVESTIGATION
(Sheet 1 of 3)

I.	Date of Core Collection: _____(1)_____(from Individual Core Collection Form)
II.	Date of Core Processing: _____(2)_____
III.	Core ID: _____(3)_____(from Individual Core Collection Form)
IV.	Primary Core: (4) Coordinate Northing (ft, NAD 83): _____(5)_____(from Individual Core Collection Form) Coordinate Easting (ft, NAD 83): _____(6)_____(from Individual Core Collection Form) Actual Penetration (ft): _____(7)_____ (from Individual Core Collection Form) Recovery (ft) During Core Collection: __(8)_____ (from Individual Core Collection Form) Recovery (%) During Core Collection: __(9)_____ (from Individual Core Collection Form) Recovery (ft) During Core Processing: __(10)_____ Recovery (%) During Core Processing: (11)_____ Recovery (%) During Core Processing = $\frac{\text{Recovery (ft) During Core Processing - Gaps (ft)}}{\text{Actual Penetration (ft)}}$ x 100

SAMPLE PROCESSING FORM
FOCUSED SEDIMENT INVESTIGATION
(Sheet 2 of 3)

I.	Date of Core Collection: (1) (from Individual Core Collection Form)
II.	Date of Core Processing: (2)
III.	Core ID: (3) (from Individual Core Collection Form)
V.	Secondary Core: (12) Coordinate Northing (ft, NAD 83): (13) (from Individual Core Collection Form) Coordinate Easting (ft, NAD 83): (14) (from Individual Core Collection Form) Actual Penetration (ft): (15) (from Individual Core Collection Form) Recovery (ft) During Core Collection: (16) (from Individual Core Collection Form) Recovery (%) During Core Collection: (17) (from Individual Core Collection Form) Recovery (ft) During Core Processing: (18) Recovery (%) During Core Processing: (19) Recovery (%) During Core Processing = $\frac{\text{Recovery (ft) During Core Processing} - \text{Gaps (ft)}}{\text{Actual Penetration (ft)}}$ x 100
VI.	Name of Person Responsible for Log: (20)

SAMPLE PROCESSING FORM
FOCUSED SEDIMENT INVESTIGATION
(Sheet 3 of 3)

Date of Core Collection: _____(1)_____(from Individual Core Collection Form)
Date of Core Processing: _____(2)_____
Core ID: _____(3)_____(from Individual Core Collection Form)

Sample ID (21)	Sample Time (24-hour) (22)	Sample Interval (ft) (23)		HCX (24)	Dioxin/Furan Congeners and Homologues (24)	Cs-137 (24)
		Top	Bottom			

Comments:(25)

SAMPLE PROCESSING FORM KEY
FOCUSED SEDIMENT INVESTIGATION
(Sheet 1 of 2)

DESCRIPTION OF ITEMS:

(1) Date of core collection (taken from the Individual Core Collection Form).

(2) Date of core processing (e.g., 1/1/2011).

(3) Core ID.

(4) The chemical analysis core is the core from which sediment is being taken for chemical analysis.

(5) Northing coordinate in feet of core collection location (taken from Individual Core Collection Form).

(6) Easting coordinate in feet of core collection location (taken from Individual Core Collection Form).

(7) Actual penetration of core into sediment (taken from the Individual Core Collection Form).

(8) Recovery (ft) at time of core collection = sediment length in core at the time of core collection (taken from the Individual Core Collection Form).

(9) Recovery (%) at time of core collection = sediment length at the time of core collection in core per actual penetration (taken from the Individual Core Collection Form).

(10) Recovery (ft) at time of core processing = sediment length in core at the time of processing. Note: the length of sediment in the core and the recovery may be different than listed on the Individual Core Collection Form due to additional consolidation of sediments within the core between the time cored and time processed.

(11) Recovery (%) during core processing = sediment length at the time of processing per actual penetration.

(12) The radiochemical analysis core is the core from which sediment is being taken for radiochemical analysis.

(13) Northing coordinate in feet of core collection location (taken from Individual Core Collection Form).

(14) Easting coordinate in feet of core collection location (taken from Individual Core Collection Form).

(15) Actual penetration of core into sediment (taken from the Individual Core Collection Form).

SAMPLE PROCESSING FORM KEY
FOCUSED SEDIMENT INVESTIGATION
(Sheet 2 of 2)

(16) Recovery (ft) at time of core collection = sediment length in core at the time of core collection (taken from the Individual Core Collection Form).

(17) Recovery (%) at time of core collection = sediment length at the time of core collection in core per actual penetration (taken from the Individual Core Collection Form).

(18) Recovery (ft) at time of core processing = sediment length in core at the time of processing.

(19) Recovery (%) at time of core processing = sediment length at the time of processing per penetration.

(20) Name of person entering information into this form.

(21) Sample ID.

(22) Time sample was removed from core (24-hour format).

(23) Sample interval = target sample interval depths multiplied by Recovery (%) at time of core processing. For example, if target sample interval is 0.5 - 1.5 feet and the Recovery (%) at time of core processing is 80%, then the sample interval would be 0.4 - 1.2 feet.

(24) Check the boxes for which analyses the sample is being submitted.

(25) Provide any pertinent comments regarding the sediment sample submitted for analyses.

SOP 8
STANDARD OPERATING PROCEDURES
CONTAINERS, PRESERVATION, HANDLING AND TRACKING OF SAMPLES FOR ANALYSIS

1.0 Scope and Application

The purpose of this document is to define the standard operating procedure (SOP) for containerizing, preserving, handling, tracking, and shipping samples collected during implementation of focused sediment investigation within the Lower Passaic River Study Area (LPRSA) in Bergen, Essex, Hudson, and Passaic Counties, New Jersey. Samples may include sediment collected or generated for chemical analysis, radiochemical analysis, and associated quality assurance (QA) analysis.

Other SOPs will be utilized with this procedure, including:

- SOP 3 – Sediment Collection Using Hand Coring Device;
- SOP 4 – Sediment Collection Using Vibracoring Device;
- SOP 5 – Core Processing;
- SOP 6 – Management and Disposal of Residuals; and
- SOP 7 – Field Documentation.

2.0 Equipment List

The following equipment list contains materials which may be needed in carrying out the procedures contained in this SOP. Not all equipment listed below may be necessary for a specific activity. Additional equipment may be required, pending field conditions.

- Personal protective equipment (PPE) and other safety equipment, as required by Focused Sediment Investigation Health and Safety Plan (ENVIRON, 2011);
- Inert packing material (e.g., foam peanuts, vermiculite, cardboard, etc.);
- Colorimetric pH test paper;
- Nitric acid (HNO_3) and pipette;
- Sample containers;
- Sample labels;
- Chain of custody;
- Ice chest(s);
- Custody seals;
- Indelible marking pens;
- Shipping tape;
- Sealable plastic bags;
- Temperature blanks (if not provided by the laboratory);
- Logbook;
- Ice or similar chilling source;
- Potassium iodide starch paper;
- Spatula;
- Sodium hydroxide (NaOH) and pipette;
- Plastic lining material; and
- Clear tape

3.0 Sample Identification and Labeling

3.1 Sampling Identification Code

Each sample will be assigned a unique alpha-numeric identification. The identification will use the following procedures:

- Two digit sample location (e.g., 01 for location number 1) preceded by a letter designation corresponding to prioritized sample locations (i.e., A for first priority, B for second priority, C for low priority);
- "SD" to indicate sediment sample;
- Three digits to indicate the depth to the top of the sample interval in inches; and
- Three digits to indicate the depth to the bottom of the sample interval in inches.

For example, the sample collected from 6 to 12 inches below the mudline at first priority sample location A2 will be designated A02-SD-006-012.

3.2 Quality Assurance Sample Identification Code

3.2.1 Field Duplicates

Laboratory-blind field duplicate samples will be collected for 20% of the field samples. The duplicate samples will be collected by alternately filling the field sample and duplicate sample containers. The following naming convention will be used for field duplicate samples:

- SD-00 to indicate a duplicate sample;
- Three-character alpha-numeric designation of the coring location; and
- Three digits to indicate the depth to the top of the sample interval in inches.

For example, a duplicate sample collected at location B01-SD-024-030 would be designated SD-00-B01-024.

3.2.2 Matrix Spike/Matrix Spike Duplicate Samples

Matrix spike/matrix spike duplicate (MS/MSD) samples will be generated by the laboratory. The laboratory will be instructed to generate the MS/MSD from sample material collected from this project for each SDG analyzed.

3.2.3 Rinsate Blanks

Rinsate blanks will be numbered by a unique 12-character string, as follows:

Characters 1 and 2: Two characters to signify a rinsate blank (RB)

Characters 3 - 10: Eight characters to describe the date using a four-digit year, two-digit month, two-digit day (e.g., YYYYMMDD).

3.3 Sample Labeling

A label will be attached to each bottle used for sampling. When practical, the project number, sample matrix, laboratory designation, and sample identification code will be typed or printed onto the label before sampling. Once affixed to the sample container, the label will be protected from water and solvents with clear tape.

4.0 Sample Containers and Preservation

4.1 Sample Containers

To ensure that the appropriate sample quantities are collected in certified, pre-cleaned containers, sample containers for this project will be supplied from commercial suppliers or laboratories. Sample containers will be cleaned to the quality control standard defined in USEPA Office of Solid Waste and Emergency Response (OSWER) Directive #9240.0-05A. The Focused Sediment Investigation Work Plan summarizes container types which will be provided for samples collected.

Prior to use, the sample containers will be visually inspected for cracks, chips, or other damage. Damaged sample containers will not be used and will be disposed of in the proper waste receptacle.

4.2 Sample Preservation

The contracted laboratory performing the analysis will provide certified, pre-cleaned containers containing a pre-determined amount of the required preservative(s) for rinsate blanks, as appropriate. In cases where field adjustment of pH is necessary, the procedures outlined below will be followed for the appropriate analysis. Sample containers for sediment will not contain preservatives.

Documentation of equipment and methods used in preservation and field-adjustment of pH will be maintained in a logbook. The chemicals and amounts used will be recorded. If refrigeration is necessary, samples will be placed on ice after collection, and shipping containers will be packed with additional ice, if needed, prior to shipment via overnight carrier.

5.0 Sample Handling and Shipping

Sample packaging and shipping will be done in accordance with applicable regulations, as described below.

1. After filling a sample container, affix cap and securely seal with clear tape and complete the sample label. Apply the label to the sample container and cover with clear tape.

2. Clean the outside of each sample container by wiping it off with a clean paper towel. Verify that residual sediment has been removed from the outside of the container, and from the area under and around the cap.

3. Seal each sample container inside a sealable plastic bag.

4. Place samples on ice or similar chilling source immediately after collection.

5. Transfer the samples to a plastic-lined ice chest which will be used as a shipping

container. Use inert packaging material (e.g., cardboard, vermiculite, etc.) to cushion the samples and minimize the potential for breakage. Seal the drains on the ice chest (if present) with shipping tape or plug the drains with silicone sealant or a similar inert substance.

6. Ice chests will contain ice or similar chilling sources sufficient to maintain a temperature of 4° Celsius (°C) inside the cooler during transport. Use sufficient ice to accommodate reasonable delays in shipment. A temperature blank provided by the analytical laboratory with each cooler will be included in the shipment.

7. Complete sample tracking documentation as described in Section 6.0 of this SOP, and place the documents in a sealable plastic bag inside the ice chest, taped to the inside of the lid. Prior to sealing for shipment, check the list of samples against the container contents to verify the presence of each sample listed on the chain of custody.

8. Secure chest lid with shipping tape by covering the entire seal with tape. Complete information on the custody seal and affix the custody seal over the taped seal.

9. Transport the shipping container directly to the laboratory, the laboratory courier, or to the overnight carrier for overnight delivery.

10. Once a core has been opened, sediment samples will be shipped by close of the same day.

11. Rinsate blank samples will also be shipped by close of the same day with the appropriate SDG.

6.0 Sample Tracking

From the time of collection through transportation, the handling of samples will follow chain of custody procedures. Completed and signed Individual Core Collection Forms will be provided by the samplers to the Sample Processing Area personnel when relinquishing the collected cores for sample processing. The Sample Processing Area personnel will sign the Individual Core Collection Form accepting custody of the cores.

A sample is considered under the sampler's custody if one or more of the criteria are met:

- sample is in the sampler's possession;
- sample is in the sampler's view after being in sampler's possession;
- sample was in the sampler's possession and then locked up to prevent tampering; or
- sample is in a designated secure area.

Samples collected for analysis will be continuously tracked in the Sample Processing Area and while in transit to the laboratory by use of the following procedures below. The Sample Processing Area will be secured (locked) with limited access.

- Individual sample bottles will be properly labeled and securely sealed before being placed in the container for shipment to the laboratory.

- Pertinent information will be entered on the chain of custody form in the field.

- The chain of custody form must include the following, as required by guidance in SW-846, Test Methods for Evaluating Solid Waste (USEPA, 1993): 1) project name; 2) signatures of samplers; 3) sample number, date and time of collection, and grab or composite sample designation; 4) signatures of individuals involved in sample transfer; and 5) if applicable, the air bill or other shipping number.

- The completed chain of custody form will be signed, dated, enclosed in a sealable plastic bag and placed in the container prior to shipment. A copy of both documents will be retained by field personnel and stored in a dedicated binder. Additional copies will be distributed as follows:

    - a copy will be faxed or emailed to the Project Manager or designee;
    - a copy will be faxed or emailed to the data validator; and
    - a copy will be faxed or emailed to the lab manager/client service representative at each laboratory being used.

- Samples will be considered in the sampler's custody while in his/her possession or within sight, or locked in a secure area prior to shipment. If the person packing the container and verifying the sample list is different than the sampler, both the sampler and the packer will sign the chain of custody form.

- Upon receipt at the laboratory, the designated laboratory sample custodian shall sign the chain of custody form indicating receipt of the incoming field samples. The samples shall be checked against the chain of custody form upon arrival at the laboratory. The receiving personnel will enter all arriving samples into a laboratory logbook. Any discrepancies between the samples and the chain of custody form(s), or any evidence of tampering with the shipping container or the custody seal will be immediately reported to the Project Manager. The sample custodian will immediately check the temperature of the cooler upon arrival at the laboratory and record the measured temperature on the chain of custody form and in a laboratory logbook.

- A completed copy of the chain of custody form shall be distributed to the following individuals on the day of sample receipt at the laboratory:

    - a copy will be faxed or emailed to the Project Manager or designee;
    - a copy will be faxed or emailed to the data validator; and
    - a copy will be faxed or emailed to the field office.

    The original shall be retained by the laboratory's sample custodian.

7.0 Documentation

7.1 Field Notes

Documentation of sample handling activities will be conducted in accordance with SOP-7 – Field Documentation. The following information should also be included in the logbook (at a minimum):

- Sample IDs collected on that day;
- Brief synopsis of types of equipment and methods used in collecting the samples; and
- Details regarding the field adjustment of preservatives, if necessary.

7.2 Chain of Custody Documentation

Samples will be tracked through chain of custody documentation as described in Section 6.0 of this SOP.

8.0 References

ENVIRON. 2011. Focused Sediment Investigation Work Plan – Lower Passaic River Study Area. August.

USEPA. 1993. SW-846, Test Methods for Evaluating Solid Waste, Third Ed., including Promulgated Update I, Chapter One.

SDG TRACKING LOG

SDG Number _____(1)_____ **SDG Open Date** _____(3)_____
Sample Matrix _____(2)_____ **SDG Close Date** _____(4)_____

Sample #	Sample ID	MS/MSD	Comments
1	(5)	(6)	(7)
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
Rinsate Blank	(8)	N/A	(9)
Trip blank	(10)	N/A	(11)

SDG TRACKING LOG KEY

(1) SDG number (sequentially numbered beginning with FSI001).

(2) Matrix of samples in this SDG (e.g., sediment).

(3) Date first sample in SDG is collected.

(4) Date last sample in SDG is collected.

(5) Sample ID.

(6) Check if a MS or MSD analysis should be performed on this sample. If a MS or MSD is to be performed, note in the "Comments" column which analysis the MS/MSD should be performed for. If the sample is not to be analyzed for a MS/MSD, then leave blank.

(7) Provide any pertinent comments regarding the sediment samples submitted for analyses.

(8) Rinsate blank ID.

(9) Provide any pertinent comments regarding the rinsate blank submitted for analyses.

(10) Trip blank ID.

(11) Provide any pertinent comments regarding the trip blank submitted for analysis.

SOP S-1
STANDARD OPERATING PROCEDURE
AIR MONITORING - PHOTOIONIZATION DETECTOR (Rae Systems MiniRAE 2000)

1.0 Scope and Application

The purpose of this Standard Operating Procedure (SOP) is to define protocols for field operations requiring the use of a photoionization detector (PID) to monitor vapor concentrations during implementation of field operations. The PID is used to detect, measure, and provide a direct reading of the total concentration of trace gases, particularly organics, in the atmosphere. The PID contains an ultraviolet light source that emits photons with an energy level high enough to ionize organics, but not high enough to ionize the primary components of atmospheric air (e.g., oxygen, nitrogen). The current produced by the ions released during ionization is measured and the corresponding concentration is displayed directly in parts per million (ppm). The concentration measurements are used to establish levels of protection and other control measures, such as action levels. The PID will not detect compounds above the ionization potential (IP) of the lamp used.

2.0 Materials

- RAE Systems MiniRAE 2000 with 10.2 eV ultraviolet lamp probe
- Silicon tubing
- Flow regulator
- Isobutylene (100 ppm) Calibration Gas

3.0 Procedure

3.1 General

Units which utilize photoionization include the MiniRAE2000, the Thermo Environmental Instruments Model 580, the Photovac PID, and HNu PI 101. For the purpose of this SOP, only the MiniRAE2000 PID procedures will be addressed.

The user should read and understand the owner's manual. A copy of the owner's manual may be found in the instrument storage shipping case. The operation of the PID is menu driven.

3.2 Operation

1. Turn the instrument on using the rocker switch on the front of the carry handle. A "warming up now, please wait" prompt will appear and the intake pump will turn on.

2. After several minutes the screen will display a "ready" prompt.

3. Check battery level.

3.3 Calibration

The instrument should be recalibrated at start of each work day or when the ambient reading will not go to zero or close to zero. Always follow instructions provided with the instrument.

1. Simultaneously press "CAL" and "N" buttons on keypad .

2. "Fresh Air Cal?" prompt will appear, press "Y+".

3. "Wait" will appear. This will measure ambient air.

4. Press "Mode" when reading is complete. "Span cal" will appear.

5. Fill tedlar bag with span gas (100 ppm Isobutylene)

6. At prompt attach tedlar bag filled with span gas. The unit will recognize the gas and begin calibration.

7. Calibration will now occur.

8. When the "Remove gas" prompt appears remove span gas.

9. Confirm that reading in ambient air is 0.0 ppm.

10. Instrument is now ready for use.

11. Recalibrate when ambient reading will not go to zero or close to zero.

12. Record all calibration activities in the Field Equipment Calibration Log and Field Log Book.

4.0 Maintenance

The sample drawn into the instrument passes over the lamp to be ionized. Dust in the atmosphere can collect on the lamp and block the transmission of UV light. This will cause a reduction in instrument reading. This problem will be detected during calibration. The lamp should be cleaned on a regular basis in accordance with the instruction manual.

As the lamp ages, the intensity of the light decreases. It will still have the same ionization energy, but the response will decline. This will be detected during calibration and adjustments can be made. When the lamp eventually burns out, it will need to be replaced.

5.0 Precautions

The energy of lamps generally available is 8.3, 8.4, 9.5, 10.2, 10.6, 10.9, 11.4, 11.7 and 11.8 eV. The lamp that is used will detect chemicals with ionization potential up to that of the lamp's. Unless otherwise specified in the health and safety plan (HASP) addendum included with this FSIWP, a PID with a 10.2 eV lamp will be utilized.

Humidity can cause two problems: 1) moisture can condense on the lamp when a cold instrument is taken into a warm moist atmosphere, reducing the available light, and 2) moisture in the air also reduces the ionization of chemicals and causes a reduction in readings.

Since an electric field is generated in the sample chamber of the instrument, radio-frequency interference from pulsed DC or AC power lines, transformers, generators, and radio wave transmission may produce an error in response. If noted or suspected, move to a different location.

6.0 References

Rae Systems MiniRAE 2000 Operator's Manual

Appendix B

Analytical Methods Standard Operating Procedures

Analytical Method SOP
No. L-1

Extraction and Analysis of Hexachloroxanthene by HRGC/HRMS, Vista 2011

SOP 41	Revision: 0	Supersedes:
EXTRACTION AND ANALYSIS OF HEXACHLOROXANTHENE BY HRMS		
Analyst Review:		
Management:		
Quality Assurance:		
Effective Date: 9 August 2011		

Revision	Description of Revision

Vista Analytical Laboratory
El Dorado Hills, CA 95762

1. PURPOSE

1.1. This procedure describes the preparation and analytical techniques used for the analysis of soil/sediment and aqueous samples for the determination of Hexachloroxanthene (HCX) by HRMS.

2. SUMMARY OF METHOD

2.1. This procedure uses matrix specific extraction, analyte specific cleanup, and HRGC/HRMS analysis techniques.

2.2. This method covers the determination of Hexachloroxanthene (HCX). The following parameter may be determined by this method:

Parameter	CAS No.
1,2,4,5,7,8-Hexachloroxanthene.	38178-99-3

2.3. Detection limits are sample-specific.

3. INTERFERENCES

3.1. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferants under the conditions of analysis by performing laboratory method blanks. Analysts should avoid using PVC gloves.

3.2. The use of high purity reagents and solvents helps minimize interference problems.

3.3. Interferants co-extracted from the sample will vary considerably from matrix to matrix.

3.4. If interferences are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination.

4. DEFINITIONS

4.1. Definitions are presented in the Glossary.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all Vista employees, including the appropriate use of Personal Protective Equipment and engineering controls.

5.2. Each chemical compound should be treated as a potential health

hazard. Exposure to these compounds should be reduced to the lowest possible level. Only highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks should handle all compounds or reagents.

5.3. Each chemical compound should be handled in well-ventilated, controlled access laboratories.

5.4. Additional health and safety information can be obtained from material safety data sheets (MSDSs) available to all personnel involved in these analyses.

5.5. In the event of a known or potential compromise to the health and safety of a Vista associate, all work must stop and the incident reported immediately to management.

6. APPARATUS AND MATERIALS

6.1. Analytical Balances, capable of reading to 0.01g and 0.0001 g

6.2. Crimp top autoinjector vials plus caps and crimp tool

6.3. Drying Oven, VWR Model 1320 or equivalent

6.4. Electrothermal electromantle six sample and 500 & 1000 mL capacity

6.5. Funnels, 100 mm

6.6. Glass columns, 160 mm x 11 mm and 200 mm x 15 mm

6.7. Glass wool

6.8. Organomation 24-Station N-Evaporator

6.9. Precleaned Glass fiber thimbles - coarse

6.10. Rotary evaporator

6.11. Round bottom flasks: 50, 100, 250, and 500 mL

6.12. Separatory funnels, typically 250 mL to 2-L size

6.13. Soxhlet/Dean-Stark (SDS) Extractor

6.14. Teflon boiling chips

6.15. Test tubes plus Teflon lined caps, 16 mm x 125 mm

6.16. Vials, Glass conical,

6.17. Volatile Organic Analysis (VOA) vials, 40 mL

6.18. Whatman GF/C, GF/D, and GF/F filters

6.19. Wiretrol II Precision Disposable Micropipettes

6.20. Zymark TurboVap II plus 250 mL tubes with 1 mL stems or equivalent

6.21. EquipmentCTC Autosampler Model A200S.

6.22. Alpha Station 500.

6.23. Neslab HX200, HX300 or HX500 Water Cooler.

6.24. HP 6890F Gas Chromatograph

6.25. 60 meter DB-5MS GC column, 0.25 mm i.d., 0.25 µm film (J&W Scientific) or equivalent

6.26. Waters Autospec Ultima Magnetic Sector High Resolution Mass Spectrometer.

6.27. Injection vial inserts, 100 µL (Sun International or equivalent)

7. REAGENTS, SOLVENTS AND STANDARDS

7.1. Reagents (Highest purity available)

7.1.1. Acid Silica Gel, 44%

7.1.2. Activated Silica Gel, kilned for ~5 hours at 550 °C, granular

7.1.3. Anhydrous sodium sulfate, kilned for ~5 hours at 550 °C, granular

7.1.4. Basic Silica Gel, 33%

7.1.5. Florisil

7.1.6. Acid Alumina

7.1.7. Hydrochloric acid, concentrated

7.1.8. Hydromatrix

7.1.9. Ottawa sand, kilned for ~5 hours at 550 °C

7.1.10. Ultra-pure nitrogen gas

7.1.11. Water, HPLC grade

7.2. Solvents

7.2.1. Tetradecane

7.2.2. Hexane

7.2.3. Methylene chloride (DCM)

7.2.4. Toluene

7.2.5. Acetone

7.3. Standards

7.3.1. All analytical standards are obtained from a certified vendor. See SOP 15 and the current spike sheet for more information.

8. QUALITY CONTROL

8.1. Method Blank (MB): Method blank is a matrix preparation that is free of native analyte that has been prepared and analyzed using the same procedures followed for the rest of the analytical batch. The method blank should simulate (as close as possible) the matrix to be extracted.

8.1.1. A method blank is run with every analytical batch or 20 samples (whichever is less).

8.1.2. For the determination of the native Hexachloroxanthene, the levels measured in the method blank must be less than the method quantitation limit or ten times lower than the concentration found in any sample within the analytical batch.

8.1.3. All samples within an analytical batch are re-extracted and analyzed if the method blank associated with that batch does not meet criteria.

8.2. Ongoing Precision and Recovery (OPR): An OPR is prepared by adding a known quantity of native standards to an interferant free matrix and used to assess method performance (precision and accuracy).

8.2.1. A 10 µ aliquot containing 4ng HCX is used for spiking.

8.2.2. The control limits are 50-150% for HCX.

8.2.3. If the OPR of an isomer is outside the recommended control than the sample and the OPR will be re-extracted and analyzed.

8.3. Matrix Spike (MS/MSD): Upon client request, a matrix spike sample is prepared by adding a known quantity of native standards to a sample matrix prior to extraction.

8.3.1. An MS/MSD is performed upon client request.

8.3.2. A 10 µ aliquot containing 4ng HCX is used for spiking.

8.3.3. The relative percent difference between MS/MSD samples should be 20%.

8.4. Duplicate Samples: Duplicate samples are two separate aliquots taken from the same source. Duplicate samples are performed upon client request.

8.4.1. A duplicate sample is performed upon client request.

8.4.2. Duplicate samples are analyzed independently to assess laboratory precision.

8.4.3. The relative percent difference from duplicate sample analyses should be less than 25%.

9. COLLECTION, PRESERVATION, AND HANDLING

9.1. Extract aqueous samples within 14 days and sediments within 14 days. Analyze within 40 days from extraction

9.2. Store all samples at 4 °C in the dark

9.3. If residual chlorine is detected in an aqueous sample, add 80 mg sodium thiosulfate per liter.

10. SAMPLE PREPARATION

10.1. Residual Chlorine Determination (aqueous only)

10.1.1. Obtain an Aquacheck strip and place it directly into a small

amount of sample in a disposable weigh boat. Move the strip back and forth for 30 seconds.

10.1.2. Check the color on the strip against the color chart on Aquacheck container.

10.1.3. If there is chlorine present, add 80 mg of sodium thiosulfate.

10.1.4. Record procedure on extraction benchsheet.

10.2. pH Determination (aqueous only)

10.2.1. Obtain a pH strip and place it directly into a small amount of sample in a disposable weigh boat. Move the strip back and forth for 30 seconds.

10.2.2. Check the color on the strip against the color chart on the pH container.

10.3. % Solids Determination

10.3.1. —ZERO‖ or—TARE‖ the balance.

10.3.2. Place a weigh boat on the balance and record the weight as—Boat Weight‖.

10.3.3. Samples are individually homogenized with a clean spoon, spoonula or spatula. Add a portion of the sample (2 – 10 g) to the weigh boat and record the weight as—Wet Wt. + Boat Wt.‖

10.3.4. Place the weigh boat plus sample in an oven at 110±5 °C for at least overnight.

10.3.5. Remove the weigh boat plus sample from the oven and allow to come to room temperature.

10.3.6. —ZERO‖ or—TARE‖ the balance.

10.3.7. Place the weigh boat plus sample on the balance and record the weight as—Residue + Boat Wt.‖

10.3.8. Calculate the percent solids by the following formula:

$$\%\text{Solids} = \frac{\text{Residue Wt.} - \text{Boat Wt.}}{\text{Wet Wt.} - \text{Boat Wt.}} \times \frac{\text{Boat Wt.}}{\text{Boat Wt.}} \times 100$$

10.3.9. For aqueous samples, if %Solid exceeds 1%, remove any rocks or stones and homogenize the sample prior to extraction. Weigh 10 grams dry-weight equivalent for extraction.

10.4. Compositing – by client request

10.4.1. Samples are individually homogenized, if necessary, with a clean spoon, spoonula or spatula. Aqueous samples should be mixed and shaken to obtain a representative sample.

10.4.2. Weigh out approximately 50 grams, or amount designate d by the client, from each individual sample and place into a pan.

10.4.3. Repeat the homogenization for each sample.

10.4.4. Place each individual sample into a new, separate container. Record the weight of each sample on the benchsheet.

10.4.5. Retain the original sample containers. The new container is given a new sample ID number and then processed through the appropriate extraction.

10.5. Sample Weight Determination

10.5.1. Volumetric: Allow sample to come to ambient temperature, mark the water meniscus on the side of the 1 L sample bottle. Once the sample has been transferred, fill the sample bottle to the mark with water and transfer to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL.

10.5.2. Gravimetric: Sample bottle including sample is placed on calibrated balance. The weight is recorded. The bottle is allowed to air-dry overnight and then re-weighed on a calibrated balance. This weight is recorded and percent solids are determined.

11. EXTRACTION PROCEDURES

11.1. Aqueous Samples

11.1.1. Record the combined weight of the bottle, cap and sample for each sample to be extracted. After the sample has

been removed from the bottle, allow it to drain overnight and reweigh it and the cap to determine the amount of sample extracted.

11.1.2. For the method blank (MB) and OPR(s), transfer ~1 liter of HPLC water into a one liter bottle for each.

- Add the appropriate volume of Internal Standard (IS) solution to a test tube containing ~1 mL of acetone. Quantitatively transfer to the aliquot of matrix with small portions of the solvent used. Add the appropriate volume of Native Standard (NS) solution to a test tube containing the IS/solvent and then quantitatively transfer to the aliquot of matrix assigned as an LCS, OPR, MS or MSD. Allow the spiked samples to equilibrate for at least 1 hour before extraction.

11.1.3. Pour the sample into a 2-liter separatory funnel. Rinse the sample container with ~60 mL of $MeCl_2$ and add it to the separatory funnel.

11.1.4. Stopper each separatory funnel and shake vigorously, with frequent venting, for 2 minutes.

11.1.5. Allow the phases to separate (centrifugation or other mechanical means may be used to facilitate separation).

11.1.6. Drain the $MeCl_2$ extract through a funnel of Na_2SO_4 into a 500 mL round bottom flask.

11.1.7. Extract the aqueous phase with two more ~60 mL portions of $MeCl_2$ (shaking 1 minute each time) and pass the extracts through the Na_2SO_4 into a round bottom.

11.1.8. Concentrate the extract to approximately 10 mLs.

11.2. Soil Samples

11.2.1. Samples are individually homogenized with a clean spoon, spoonula or spatula. Weigh the sample (nominal 10 g dry weight equivalent) directly into an analyte-free thimble, carefully breaking up any large lumps of sample.

11.2.2. Add the appropriate volume of IS and NS solutions directly to the aliquot of matrix.

11.2.3. Assemble the SDS apparatus, and add a fresh charge of

DCM to the receiver and reflux flask. Apply power to the heating mantle to begin refluxing.

11.2.4. Reflux the sample for a total of 16 hours. Cool and disassemble the apparatus.

11.2.5. Add CRS to the extract.

11.2.6. Concentrate the extracts using the rotary evaporator. Exchange twice with 50 mLs of hexane. Bring to < 2mL of hexane.

12. CLEANUP PROCED URES

12.1. Silica Gel Column Preparation

12.1.1. Pack an 11 mm. id. x 160 mm. column as per Figure 1.

12.1.2. Pre-rinse the column with 20 mL of hexane. Discard the rinsate.

12.1.3. Quantitatively transfer the sample extract onto the column using a disposable pipet. Rinse with additional hexane and add to the column and collect the eluate.

12.1.4. Just prior to the exposure of the sodium sulfate layer to air, add 25 mL of hexane. After the hexane has passed, elute with 35 mL of 40% MeCl2/hexane. Continue collection of the eluate into a 100 mL round bottom flask.

12.1.5. Roto-evaporate the eluate to less than 5 mL. Quantitatively transfer to an 8 mL test tube, using a hexane rinse. Concentrate appropriately.

12.2. Acid Base Silica Gel/Acid Alumina (ABSG/AA) (optional)

12.2.1. Prepare the column as depicted in Figure 1.

12.2.2. Rinse the ABSG column with ~60 mL hexane, discard the eluate. Rinse the AA column with ~30 mL of DCM and then ~30 mL hexane.

12.2.3. Position the ABSG column so that it elutes directly onto the Acid Alumina column.

12.2.4. Transfer the extract to the ABSG column with 2-4 small portions of hexane.

12.2.5. When the extract reaches the sodium sulfate, add 150 mL

of hexane.

12.2.6. When all of the ABSG eluate has passed through the Acid Alumina column, remove the ABSG column, discard all the eluates.

12.2.7. Elute the Acid Alumina column with ~50 mL of 20% MeCl2:hexane, collect the eluate.

12.2.8. Add 100 µ tetradecane and concentrate to the tetradecane at 50°C (only if proceeding to Florisil).

12.3. Florisil (F) (optional)

12.3.1. Prepare the column as depicted in Figure 2.

12.3.2. After removing the florisil jar from the oven, allow the florisil to cool ~ 10 minutes before weighing it out.

12.3.3. Rinse the column with ~50 mL of DCM, then ~50 mL of hexane, discard the eluate.

12.3.4. Transfer the extract to the column with 2-4 small portions of hexane, discard the eluate.

12.3.5. Elute the column with ~30 mL of hexane, discard eluate.

12.3.6. Elute the column with ~50 mL of MeCl2, collect the eluate.

12.3.7. Concentrate the eluate appropriately.

13. ADJUST TO FINAL VOLUME

13.1. Using hexane, quantitatively transfer the concentrated eluate to a conical vial that contains the Recovery Standard (RS) and 10 µ of tetradecane.

13.2. Using nitrogen blow down, concentrate to the tetradecane.

13.3. Rinse the walls of the conical with hexane, concentrate down to the tetradecane.

13.4. Using a 10- 20 µ Wiretrol, transfer the tetradecane to an insert in a crimp top autoinjector vial and then cap.

14. GC/MS ANALYSIS

14.1. Analyze samples with selected ion monitoring.

14.2. The ratio of the integrated ion currents of both the exact m/z's monitored must be 1.05 – 1.43.

14.3. Recovery of each internal standard versus the recovery standard must be between 25 – 150% or have a signal to noise ratio ≥ 2.5:1 for natives and > 10:1 for labeled compounds.

15. CALIBRATION

15.1. Initial Calibration

15.1.1. An initial calibration curve is created to demonstrate the linearity of the HRMS system over the calibration range. An initial calibration is repeated whenever a new set of spiking calibration standards are created or whenever the continuing calibration falls outside the acceptance criteria.

15.1.2. Each calibration standard contains HCX. Calibration standard solutions are presented in Table 2.

15.1.3. One internal standard and one recovery standard are used to improve quantitation.

15.1.4. See Table 2 for calibration range.

15.1.5. 2 µL maximum injection of standards are made to create an initial calibration curve whenever the continuing calibration check falls outside the acceptable relative response factor window.

15.1.6. An initial calibration curve is accepted if the following criteria are met:

1.) The signal to noise ratio (s/n) exceeds 10:1 for all ions monitored.

2.) The ion abundance ratio measurements are within ± 15% of the theoretical ratio.

3.) The %RSD for the mean response factors must be within ±20% for the native standards and within ±35% for internal standards.

15.1.7. If the criteria are not achieved, a new initial calibration curve must be re-injected or prepared.

15.2. Continuing Calibration

15.2.1. A verification (VER) standard from the initial calibration curve (CS3) containing is injected at the beginning of an analytical 12-hour sequence. The following criteria must be met:

15.2.2. The percent deviation recoveries for the native compounds are 70-130% and 50-150% for labeled compounds.

15.2.3. The ion ratios are within the criteria listed in Table 1. If the ratios do not meet the acceptance criteria, then the instrument must be recalibrated and the affected samples should be reanalyzed.

15.2.4. The signal to noise ratio (s/n) exceeds 10:1 for all ions monitored. If the s/n ratio is not met, then associated extracts should be re-analyzed.

15.3. Qualitative Determination

15.3.1. To identify a chromatographic peak as a HCX, it must meet the following criteria:

1) The signals for the two exact m/zs being monitored must be present and must maximize within ± seconds of one another.

2) The signal- to-noise ratio (S/N) of each of the two exact m/zs must be ≥ .5:1 for a sample extract.

3) The ion abundance ratios must be within the limits established for the homologous series (Table 1).

4) The relative retention time of HCX must be within 1.044-1.086 seconds of ^{13}C-1,2,3,7,8,9-HxCDF.

15.3.2. Quantitative Determination

15.3.3. Quantitate the HCX peaks from the response relative to the appropriate internal standard.

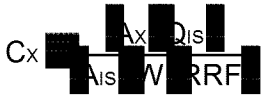
15.3.4. Recovery of each internal standard versus the recovery standard must be 25-150%.

15.3.5. Recoveries below the limits may be accepted if the signal to noise is >10:1. If the signal to noise is not >10:1, samples must be re-extracted and re-analyzed or the data must be qualified.

15.3.6. If a chromatographic peak saturates the detector, a dilution of the extract must be analyzed.

16. Calculations

16.1. The concentrations for HCX compounds are calculated by using the formula:



Where:

C_X = *Concentration of unlabeled HCX congeners (or group of coeluting isomers within an homologous series),*

A_X = *Sum of the integrated ion abundances of the quantitation ions for unlabeled HCX*

A_{IS} = *Sum of the integrated ion abundances of the quantitation ion for the labeled internal standards,*

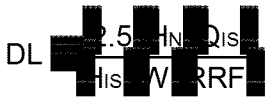
Q_{IS} = *Quantity, in pg, of the internal standard added to the sample before extraction,*

W = *Weight of the sample (solid, dry weight or liquid)*

DW = *Sample wt.* [redacted] *%solids/100*

RRF = *Calculated relative response factor for the analyte.*

16.2. The detection limits can be calculated using the following formula:



Where:

DL = *Sample specific estimated detection limit,*

H_N = *Noise height (peak to peak),*

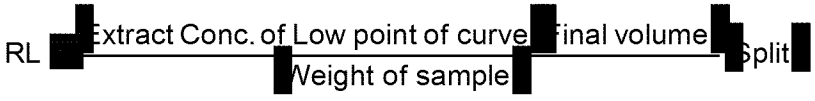
H_{IS} = *Peak height of the internal standard,*

Q_{is} = *Quantity, in pg, of the internal standard added to the sample before extraction,*

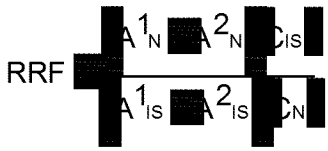
W = *Weight of the sample (solid or liquid), and*

RRF = *Calculated relative response factor for the analyte.*

16.3. The reporting limits can be calculated using the following formula:



16.4. The Relative Response factor can be calculated using the following formula:



Where:

$A1_N$, $A2_N$ = *Areas of the primary and secondary m/zs for the native compound*

$A1_{IS}$, $A2_{IS}$ = *Areas of the primary and secondary m/zs for the labeled compound.*

C_{IS} = *Concentration of the labeled compound in the calibration standard.*

C_N = *Concentration of the native compound in the calibration standard*

17. POLLUTION PREVENTION

17.1. The techniques used in this method are amenable to solvent recovery, and it is recommended that the laboratory recover solvents wherever feasible.

17.2. Standards should be prepared in volumes consistent with laboratory use to minimize disposal of standards.

18. WASTE MANAGEMENT

18.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. Safety officer should be contacted if additional information is required.

18.2. The laboratory waste management is in compliance with all federal, state, and local regulations to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations.

19. REFERENCES

19.1. EPA Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS, United States Office of Water, EPA No. EPA 821-R-00-002, Environmental Protection Agency (4303), December 1999

19.2. USEPA Method 1613, Revision B, Dated October 1994.

Figure 1

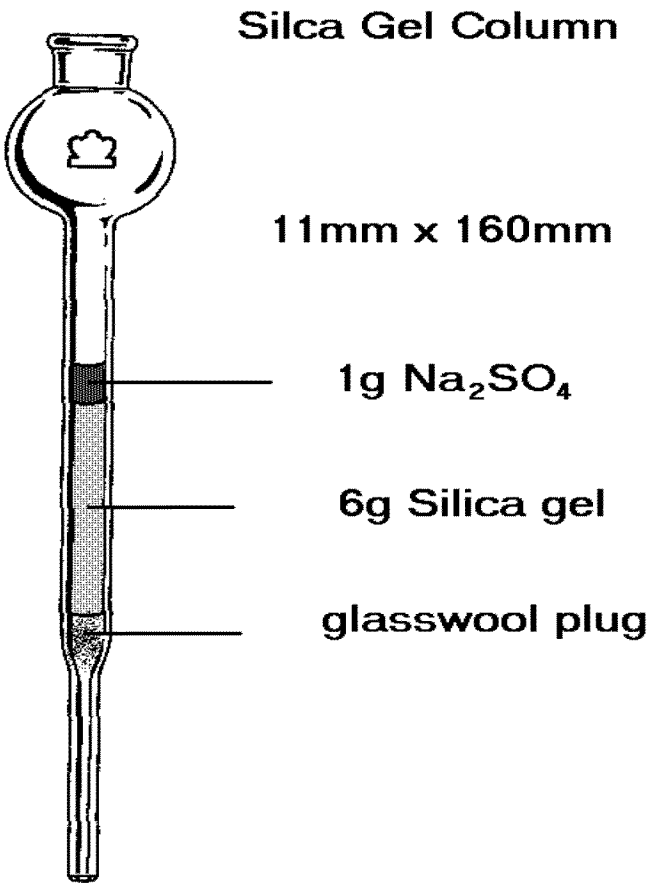


Figure 2

Acid Base Silica Gel/Acid Alumina (ABSG/AA)

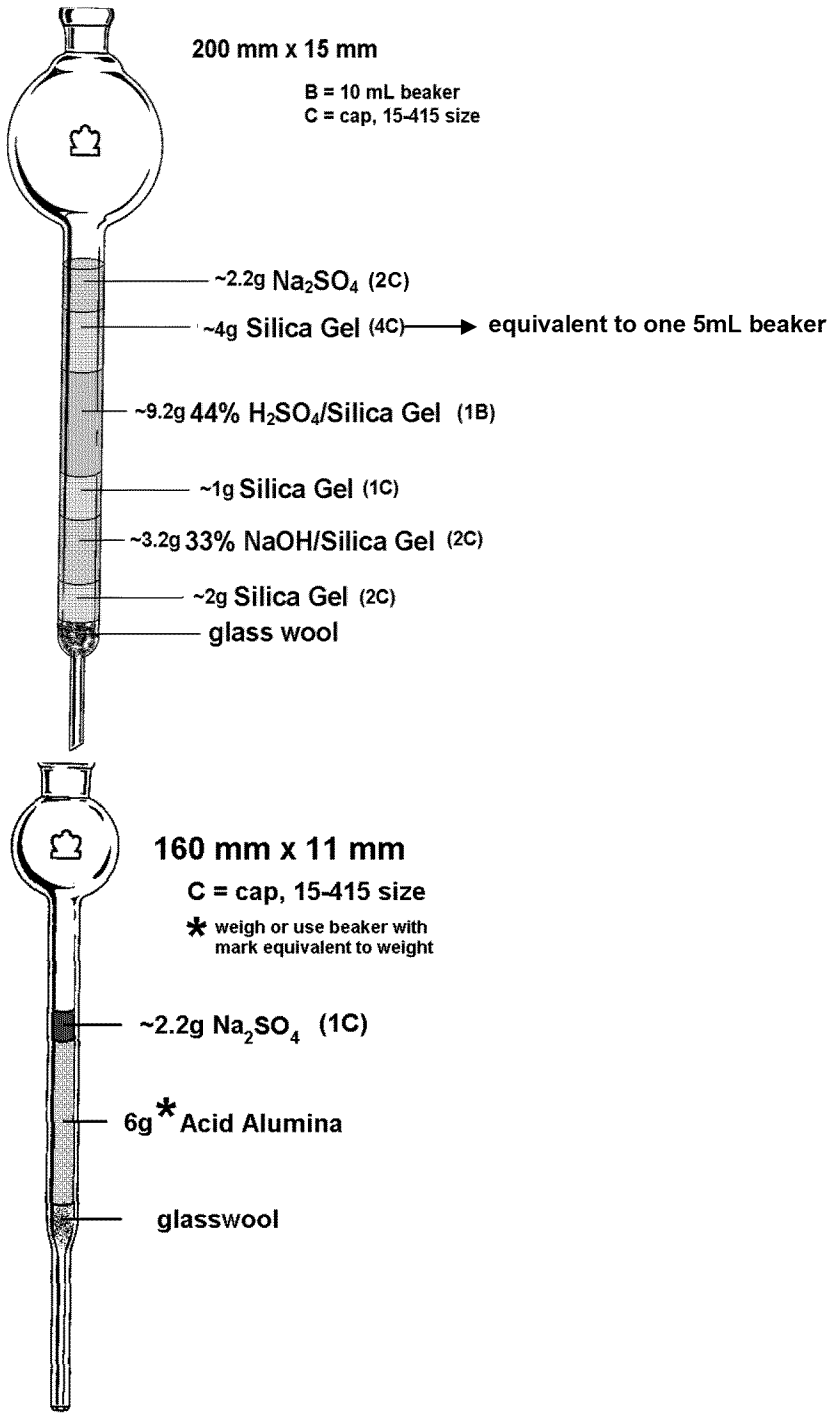


Figure 3

Florisil

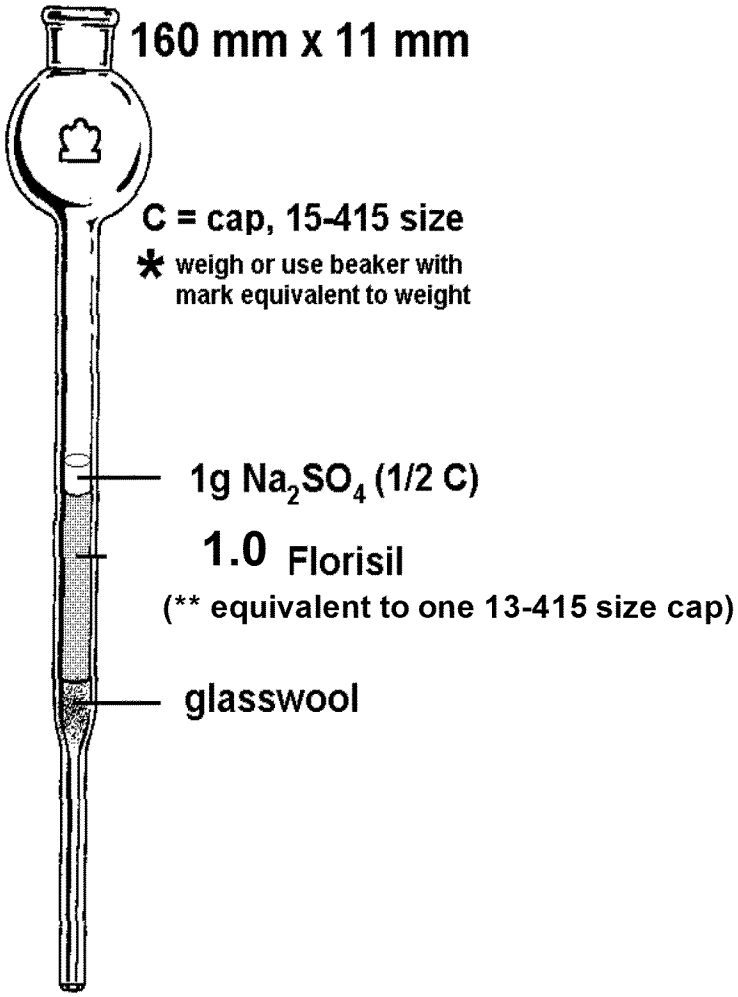


Table 1A

Hexachloroxanthene

Number of Chlorine Atoms	Exact m/z	Theoretical Ratio	Control Limits	
			Lower	Upper
6	387.8364/389.8334	1.24	1.05	1.43

(1) Represents ± 5% windows around the theoretical ion abundance ratios.

Table 1B

Standards

Labeled Compound	Exact m/z	Theoretical Ratio	Control Limits	
			Lower	Upper
^{13}C-1,2,3,7,8,9-HxCDF	383.8639/385.8610	0.51	0.43	0.59
^{13}C-1,2,3,4,6,9-HxCDF	383.8639/385.8610	0.51	0.43	0.59

Table 2

Compound		Calibration Solutions (ng/mL)					
Native Compound	**CS0**	**CS1**	**CS2**	**CS3***	**CS4**	**CS5**	**CS6**
Hexachloroxanthene	10	25	100	500	1000	2000	4000
Labeled Compound							
^{13}C-1,2,3,7,8,9-HxCDF	100	100	100	100	100	100	100
Recovery Standard							
^{13}C-1,2,3,4,6,9-HxCDF	100	100	100	100	100	100	100

* Calibration Verification Solution

Table 3

Congener	VER	IPR		OPR %	Labeled compound recovery in samples %
		RSD %	Ave %		
1,2,4,5,7,8-HxCX	70-130	40	60-140	50-150	
^{13}C-1,2,3,7,8,9-HxCDF	50-150	50	35-135	30-140	25-150

Glossary

Calibration Standard (CAL) — A solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration.

Calibration Verification Standard (VER) — The mid-point calibration standard (CS3) that is used in to verify calibration. See Table 2.

CS0, CS1, CS2, CS3, CS4, CS5 — See Calibration standards and Table 2.

Field Blank — An aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

GC — Gas chromatograph or gas chromatography.

HRGC — High resolution GC.

HRMS — High resolution MS.

IPR — Initial precision and recovery; four aliquots of the diluted PAR standard analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.

Laboratory Blank — See method blank.

Laboratory Control sample (LCS) — See ongoing precision and recovery standard (OPR).

Laboratory Reagent Blank — See method blank.

May — This action, activity, or procedural step is neither required nor prohibited.

May Not — This action, activity, or procedural step is prohibited.

Method Blank — An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

Minimum Level (ML) — The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

MS — Mass spectrometer or mass spectrometry.

Must — This action, activity, or procedural step is required.

OPR — Ongoing precision and recovery sample (OPR); a laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

PFK — Perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

Preparation Blank — See method blank.

Primary Dilution Standard — A solution containing the specified analytes that is purchased or prepared from stock solutions and diluted as needed to prepare calibration solutions and other solutions.

Quality Control Check Sample (QCS) — A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

Reagent Water — Water demonstrated to be free from the analytes of interest and potentially interfering substances at the method detection limit for the analyte.

Relative Standard Deviation (RSD) — The standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

RSD — See relative standard deviation.

Should — This action, activity, or procedural step is suggested but not required.

SICP — Selected ion current profile; the line described by the signal at an exact m/z.

Stock Solution — A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

VER — See calibration verification standard.

Analytical Method SOP
No. L-2

USEPA 1613B

Method 1613

Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS

October 1994

U.S. Environmental Protection Agency
Office of Water
Engineering and Analysis Division (4303)
401 M Street S.W.
Washington, D.C. 20460

Acknowledgments

This method was prepared under the direction of William A. Telliard of the Engineering and Analysis Division within the EPA Office of Water. This document was prepared under EPA Contract No. 68-C3-0337 by DynCorp Environmental Services Division with assistance from its subcontractor Interface, Inc.

Disclaimer

This method has been reviewed by the Engineering and Analysis Division, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Introduction

Method 1613 was developed by the United States Environmental Protection Agency's Office of Science and Technology for isomer-specific determination of the 2,3,7,8-substituted, tetra- through octa-chlorinated, dibenzo-*p*-dioxins and dibenzofurans in aqueous, solid, and tissue matrices by isotope dilution, high resolution capillary column gas chromatography (HRGC)/high resolution mass spectrometry (HRMS).

Questions concerning this method or its application should be addressed to:

W.A. Telliard
US EPA Office of Water
Analytical Methods Staff
Mail Code 4303
401 M Street, SW
Washington, D.C. 20460
202/260-7120

Requests for additional copies should be directed to:

Water Resource Center
Mail Code RC-4100
401 M Street, SW
Washington, D.C. 20460
202/260-7786 or 202/260-2814

Method 1613, Revision B
Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS

1.0 Scope and Application

1.1 This method is for determination of tetra- through octa-chlorinated dibenzo-*p*-dioxins (CDDs) and dibenzofurans (CDFs) in water, soil, sediment, sludge, tissue, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The method is for use in EPA's data gathering and monitoring programs associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act. The method is based on a compilation of EPA, industry, commercial laboratory, and academic methods (References 1-6).

1.2 The seventeen 2,3,7,8-substituted CDDs/CDFs listed in Table 1 may be determined by this method. Specifications are also provided for separate determination of 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachloro-dibenzofuran (2,3,7,8-TCDF).

1.3 The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The minimum levels (MLs) in Table 2 are the levels at which the CDDs/CDFs can be determined with no interferences present. The Method Detection Limit (MDL) for 2,3,7,8-TCDD has been determined as 4.4 pg/L (parts-per-quadrillion) using this method.

1.4 The GC/MS portions of this method are for use only by analysts experienced with HRGC/HRMS or under the close supervision of such qualified persons. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

1.5 This method is "performance-based". The analyst is permitted to modify the method to overcome interferences or lower the cost of measurements, provided that all performance criteria in this method are met. The requirements for establishing method equivalency are given in Section 9.1.2.

1.6 Any modification of this method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

2.0 Summary of Method

Flow charts that summarize procedures for sample preparation, extraction, and analysis are given in Figure 1 for aqueous and solid samples, Figure 2 for multi-phase samples, and Figure 3 for tissue samples.

2.1 Extraction

2.1.1 Aqueous samples (samples containing less than 1% solids)ÐStable isotopically labeled analogs of 15 of the 2,3,7,8-substituted CDDs/CDFs are spiked into a 1 L sample, and the sample is extracted by one of three procedures:

2.1.1.1 Samples containing no visible particles are extracted with methylene chloride in a separatory funnel or by the solid-phase extraction technique summarized in Section 2.1.1.3. The extract is concentrated for cleanup.

2.1.1.2 Samples containing visible particles are vacuum filtered through a glass-fiber filter. The filter is extracted in a Soxhlet/Dean-Stark (SDS) extractor (Reference 7), and the filtrate is extracted with methylene chloride in a separatory funnel. The methylene chloride extract is concentrated and combined with the SDS extract prior to cleanup.

2.1.1.3 The sample is vacuum filtered through a glass-fiber filter on top of a solid-phase extraction (SPE) disk. The filter and disk are extracted in an SDS extractor, and the extract is concentrated for cleanup.

2.1.2 Solid, semi-solid, and multi-phase samples (but not tissue)ÐThe labeled compounds are spiked into a sample containing 10 g (dry weight) of solids. Samples containing multiple phases are pressure filtered and any aqueous liquid is discarded. Coarse solids are ground or homogenized. Any non-aqueous liquid from multi-phase samples is combined with the solids and extracted in an SDS extractor. The extract is concentrated for cleanup.

2.1.3 Fish and other tissueÐThe sample is extracted by one of two procedures:

2.1.3.1 Soxhlet or SDS extractionÐA 20 g aliquot of sample is homogenized, and a 10 g aliquot is spiked with the labeled compounds. The sample is mixed with sodium sulfate, allowed to dry for 12-24 hours, and extracted for 18-24 hours using methylene chloride:hexane (1:1) in a Soxhlet extractor. The extract is evaporated to dryness, and the lipid content is determined.

2.1.3.2 HCl digestionÐA 20 g aliquot is homogenized, and a 10 g aliquot is placed in a bottle and spiked with the labeled compounds. After equilibration, 200 mL of hydrochloric acid and 200 mL of methylene chloride:hexane (1:1) are added, and the bottle is agitated for 12-24 hours. The extract is evaporated to dryness, and the lipid content is determined.

2.2 After extraction, $^{37}Cl_4$-labeled 2,3,7,8-TCDD is added to each extract to measure the efficiency of the cleanup process. Sample cleanups may include back-extraction with acid and/or base, and gel permeation, alumina, silica gel, Florisil and activated carbon chromatography. High-performance liquid chromatography (HPLC) can be used for further isolation of the 2,3,7,8-isomer or other specific isomers or congeners. Prior to the cleanup procedures cited above, tissue extracts are cleaned up using an anthropogenic isolation column, a batch silica gel adsorption, or sulfuric acid and base back-extraction, depending on the tissue extraction procedure used.

2.3 After cleanup, the extract is concentrated to near dryness. Immediately prior to injection, internal standards are added to each extract, and an aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high-resolution (≥10,000) mass spectrometer. Two exact m/z's are monitored for each analyte.

2.4 An individual CDD/CDF is identified by comparing the GC retention time and ion-abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundanceratio of the two exact m/z's. The non-2,3,7,8substituted isomers and congeners are identified when retention times and ion-abundanceratios agree within predefined limits. Isomer specificity for 2,3,7,8-TCDD and 2,3,7,8-TCDFis achieved using GC columns that resolve these isomers from the other tetra-isomers.

2.5 Quantitative analysis is performed using selected ion current profile (SICP) areas, in one of three ways:

2.5.1 For the 15 2,3,7,8-substituted CDDs/CDFs with labeled analogs (see Table 1), the GC/MS system is calibrated, and the concentration of each compound is determined using the isotope dilution technique.

2.5.2 For 1,2,3,7,8,9-HxCDD,OCDF, and the labeled compounds, the GC/MS system is calibrated and the concentration of each compound is determined using the internal standard technique.

2.5.3 For non-2,3,7,8-substitutedisomers and for all isomers at a given level of chlorination (i.e., total TCDD), concentrations are determined using response factors from calibration of the CDDs/CDFs at the same level of chlorination.

2.6 The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and GC/MS systems.

3.0 Definitions

Definitions are given in the glossary at the end of this method.

4.0 Contamination and Interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms (References 8-9). Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinse.

4.2 Proper cleaning of glassware is extremely important, because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption on the glass surface.

4.2.1 Glassware should be rinsed with solvent and washed with a detergent solution as soon after use as is practical. Sonication of glassware containing a detergent solution for approximately 30 seconds may aid in cleaning. Glassware with

removable parts, particularly separatory funnels with fluoropolymer stopcocks, must be disassembled prior to detergent washing.

4.2.2 After detergent washing, glassware should be rinsed immediately, first with methanol, then with hot tap water. The tap water rinse is followed by another methanol rinse, then acetone, and then methylene chloride.

4.2.3 Do not bake reusable glassware in an oven as a routine part of cleaning. Baking may be warranted after particularly dirty samples are encountered but should be minimized, as repeated baking of glassware may cause active sites on the glass surface that will irreversibly adsorb CDDs/CDFs.

4.2.4 Immediately prior to use, the Soxhlet apparatus should be pre-extracted with toluene for approximately three hours (see Sections 12.3.1 through 12.3.3). Separatory funnels should be shaken with methylene chloride/toluene (80/20 mixture) for two minutes, drained, and then shaken with pure methylene chloride for two minutes.

4.3 All materials used in the analysis shall be demonstrated to be free from interferences by running reference matrix method blanks initially and with each sample batch (samples started through the extraction process on a given 12-hour shift, to a maximum of 20 samples).

4.3.1 The reference matrix must simulate, as closely as possible, the sample matrix under test. Ideally, the reference matrix should not contain the CDDs/CDFs in detectable amounts, but should contain potential interferents in the concentrations expected to be found in the samples to be analyzed. For example, a reference sample of human adipose tissue containing pentachloronaphthalene can be used to exercise the cleanup systems when samples containing pentachloronaphthalene are expected.

4.3.2 When a reference matrix that simulates the sample matrix under test is not available, reagent water (Section 7.6.1) can be used to simulate water samples; playground sand (Section 7.6.2) or white quartz sand (Section 7.3.2) can be used to simulate soils; filter paper (Section 7.6.3) can be used to simulate papers and similar materials; and corn oil (Section 7.6.4) can be used to simulate tissues.

4.4 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the CDDs/CDFs. The most frequently encountered interferences are chlorinated biphenyls, methoxy biphenyls, hydroxydiphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and pesticides. Because very low levels of CDDs/CDFs are measured by this method, the elimination of interferences is essential. The cleanup steps given in Section 13 can be used to reduce or eliminate these interferences and thereby permit reliable determination of the CDDs/CDFs at the levels shown in Table 2.

4.5 Each piece of reusable glassware should be numbered to associate that glassware with the processing of a particular sample. This will assist the laboratory in tracking possible sources of contamination for individual samples, identifying glassware associated with

highly contaminated samples that may require extra cleaning, and determining when glassware should be discarded.

4.6 Cleanup of tissueÐThe natural lipid content of tissue can interfere in the analysis of tissue samples for the CDDs/CDFs. The lipid contents of different species and portions of tissue can vary widely. Lipids are soluble to varying degrees in various organic solvents and may be present in sufficient quantity to overwhelm the column chromatographic cleanup procedures used for cleanup of sample extracts. Lipids must be removed by the lipid removal procedures in Section 13.7, followed by alumina (Section 13.4) or Florisil (Section 13.8), and carbon (Section 13.5) as minimum additional cleanup steps. If chlorodiphenyl ethers are detected, as indicated by the presence of peaks at the exact m/z's monitored for these interferents, alumina and/or Florisil cleanup must be employed to eliminate these interferences.

5.0 Safety

5.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level.

5.1.1 The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. It is soluble in water to approximately 200 ppt and in organic solvents to 0.14%. On the basis of the available toxicological and physical properties of 2,3,7,8-TCDD, all of the CDDs/CDFs should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.

5.1.2 It is recommended that the laboratory purchase dilute standard solutions of the analytes in this method. However, if primary solutions are prepared, they shall be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator shall be worn when high concentrations are handled.

5.2 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in these analyses. It is also suggested that the laboratory perform personal hygiene monitoring of each analyst who uses this method and that the results of this monitoring be made available to the analyst. Additional information on laboratory safety can be found in References 10-13. The references and bibliography at the end of Reference 13 are particularly comprehensive in dealing with the general subject of laboratory safety.

5.3 The CDDs/CDFs and samples suspected to contain these compounds are handled using essentially the same techniques employed in handling radioactive or infectious materials. Well-ventilated,controlled access laboratories are required. Assistance in evaluating the health hazards of particular laboratory conditions may be obtained from certain consulting laboratories and from State Departments of Health or Labor, many of which have an industrial health service. The CDDs/CDFs are extremely toxic to laboratory animals. Each laboratory must develop a strict safety program for handling these compounds. The practices in References 2 and 14 are highly recommended.

5.3.1 FacilityÐWhen finely divided samples (dusts, soils, dry chemicals) are handled, all operations (including removal of samples from sample containers, weighing, transferring, and mixing) should be performed in a glove box demonstrated to be leak tight or in a fume hood demonstrated to have adequate air flow. Gross losses to the laboratory ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in the case of an accident.

5.3.2 Protective equipmentÐDisposable plastic gloves, apron or lab coat, safety glasses or mask, and a glove box or fume hood adequate for radioactive work should be used. During analytical operations that may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters. Eye protection equipment (preferably full face shields) must be worn while working with exposed samples or pure analytical standards. Latex gloves are commonly used to reduce exposure of the hands. When handling samples suspected or known to contain high concentrations of the CDDs/CDFs, an additional set of gloves can also be worn beneath the latex gloves.

5.3.3 TrainingÐWorkers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

5.3.4 Personal hygieneÐHands and forearms should be washed thoroughly after each manipulation and before breaks (coffee, lunch, and shift).

5.3.5 ConfinementÐIsolated work areas posted with signs, segregated glassware and tools, and plastic absorbent paper on bench tops will aid in confining contamination.

5.3.6 Effluent vaporsÐThe effluents of sample splitters from the gas chromatograph (GC) and from roughing pumps on the mass spectrometer (MS) should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boilingalcohols to condense CDD/CDF vapors.

5.3.7 Waste HandlingÐGood technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors and other personnel must be trained in the safe handling of waste.

5.3.8 Decontamination

5.3.8.1 Decontamination of personnelÐUse any mild soap with plenty of scrubbing action.

5.3.8.2 Glassware, tools, and surfacesÐChlorothene NU Solvent is the least toxic solvent shown to be effective. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with any detergent and water. If glassware is first rinsed with solvent, then the dish water may be disposed of in the sewer. Given the cost of disposal, it is prudent to minimize solvent wastes.

5.3.9 LaundryÐClothing known to be contaminated should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the

hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows of the potential problem. The washer should be run through a cycle before being used again for other clothing.

5.3.10 Wipe testsÐA useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper. Extraction and analysis by GC with an electron capture detector (ECD) can achieve a limit of detection of 0.1 µg per wipe; analysis using this method can achieve an even lower detection limit. Less than 0.1 µg per wipe indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 µg on a wipe constitutes an acute hazard and requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed.

5.3.11 Table or wrist-action shakerÐThe use of a table or wrist-action shaker for extraction of tissues presents the possibility of breakage of the extraction bottle and spillage of acid and flammable organic solvent. A secondary containment system around the shaker is suggested to prevent the spread of acid and solvents in the event of such a breakage. The speed and intensity of shaking action should also be adjusted to minimize the possibility of breakage.

6.0 Apparatus and Materials

NOTE: *Brand names, suppliers, and part numbers are for illustration purposes only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this method is the responsibility of the laboratory.*

6.1 Sampling Equipment for Discrete or Composite Sampling

6.1.1 Sample bottles and caps

6.1.1.1 Liquid samples (waters, sludges and similar materials containing 5% solids or less)ÐSample bottle, amber glass, 1.1 L minimum, with screw cap.

6.1.1.2 Solid samples (soils, sediments, sludges, paper pulps, filter cake, compost, and similar materials that contain more than 5% solids)ÐSample bottle, wide mouth, amber glass, 500 mL minimum.

6.1.1.3 If amber bottles are not available, samples shall be protected from light.

6.1.1.4 Bottle capsÐThreaded to fit sample bottles. Caps shall be lined with fluoropolymer.

6.1.1.5 Cleaning

6.1.1.5.1 Bottles are detergent water washed, then solvent rinsed before use.

6.1.1.5.2 Liners are detergent water washed, rinsed with reagent water (Section 7.6.1) followed by solvent, and baked at approximately 200°C for a minimum of 1 hour prior to use.

6.1.2 Compositing equipmentÐAutomatic or manual compositing system incorporating glass containers cleaned per bottle cleaning procedure above. Only glass or fluoropolymer tubing shall be used. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used in the pump only. Before use, the tubing shall be thoroughly rinsed with methanol, followed by repeated rinsing with reagent water to minimize sample contamination. An integrating flow meter is used to collect proportional composite samples.

6.2 Equipment for Glassware CleaningÐLaboratory sink with overhead fume hood.

6.3 Equipment for Sample Preparation

6.3.1 Laboratory fume hood of sufficient size to contain the sample preparation equipment listed below.

6.3.2 Glove box (optional).

6.3.3 Tissue homogenizerÐVirTis Model 45 Macro homogenizer (American Scientific Products H-3515,or equivalent) with stainless steel Macro-shaftand Turbo-shear blade.

6.3.4 Meat grinderÐHobart, or equivalent, with 3-5mm holes in inner plate.

6.3.5 Equipment for determining percent moisture

6.3.5.1 OvenÐCapable of maintaining a temperature of 110 ±5°C.

6.3.5.2 Dessicator.

6.3.6 Balances

6.3.6.1 AnalyticalÐCapable of weighing 0.1 mg.

6.3.6.2 Top loadingÐCapable of weighing 10 mg.

6.4 Extraction Apparatus

6.4.1 Water samples

6.4.1.1 pH meter, with combination glass electrode.

6.4.1.2 pH paper, wide range (Hydrion Papers, or equivalent).

6.4.1.3 Graduated cylinder, 1 L capacity.

6.4.1.4 Liquid/liquid extractionÐSeparatory funnels, 250 mL, 500 mL, and 2000 mL, with fluoropolymer stopcocks.

6.4.1.5 Solid-phaseextraction

6.4.1.5.1 One liter filtration apparatus, including glass funnel, glass frit support, clamp, adapter, stopper, filtration flask, and vacuum tubing (Figure 4). For wastewater samples, the apparatus should accept 90 or 144 mm disks. For drinking water or other samples containing low solids, smaller disks may be used.

6.4.1.5.2 Vacuum source capable of maintaining 25 in. Hg, equipped with shutoff valve and vacuum gauge.

6.4.1.5.3 Glass-fiber filterÐWhatman GMF 150 (or equivalent), 1 micron pore size, to fit filtration apparatus in Section 6.4.1.5.1.

6.4.1.5.4 Solid-phase extraction disk containing octadecyl (C_{18}) bonded silica uniformly enmeshed in an inert matrixÐFisher Scientific 14-378F (or equivalent), to fit filtration apparatus in Section 6.4.1.5.1.

6.4.2 Soxhlet/Dean-Stark (SDS) extractor (Figure 5)ÐFor filters and solid/sludge samples.

6.4.2.1 SoxhletÐ50 mm ID, 200 mL capacity with 500 mL flask (Cal-Glass LG-6900,or equivalent, except substitute 500 mL round-bottomflask for 300 mL flat-bottomflask).

6.4.2.2 ThimbleÐ43 x 123 to fit Soxhlet (Cal-GlassLG-6901-122or equivalent).

6.4.2.3 Moisture trapÐDean Stark or Barret with fluoropolymer stopcock, to fit Soxhlet.

6.4.2.4 Heating mantleÐHemispherical, to fit 500 mL round-bottom flask (Cal-GlassLG-8801-112or equivalent).

6.4.2.5 Variable transformerÐPowerstat (or equivalent), 110 volt, 10 amp.

6.4.3 Apparatus for extraction of tissue.

6.4.3.1 Bottle for extraction (if digestion/extraction using HCl is used)Ð 500-600mL wide-mouthclear glass, with fluoropolymer-linedcap.

6.4.3.2 Bottle for back-extractionÐ100-200 mL narrow-mouth clear glass with fluoropolymer-linedcap.

6.4.3.3 Mechanical shakerÐWrist-action or platform-type rotary shaker that produces vigorous agitation (Sybron Thermolyne Model LE "Big Bill" rotator/shaker, or equivalent).

6.4.3.4 Rack attached to shaker table to permit agitation of four to nine samples simultaneously.

6.4.4 BeakersÐ400-500 mL.

6.4.5 SpatulasÐStainless steel.

6.5 Filtration Apparatus

6.5.1 Pyrex glass woolÐSolvent-extracted by SDS for three hours minimum.

NOTE: *Baking glass wool may cause active sites that will irreversibly adsorb CDDs/CDFs.*

6.5.2 Glass funnelÐ125-250 mL.

6.5.3 Glass-fiber filter paperÐWhatman GF/D (or equivalent), to fit glass funnel in Section 6.5.2.

6.5.4 Drying columnÐ15-20 mm ID Pyrex chromatographic column equipped with coarse-glass frit or glass-wool plug.

6.5.5 Buchner funnelÐ15 cm.

6.5.6 Glass-fiber filter paperÐto fit Buchner funnel in Section 6.5.5.

6.5.7 Filtration flasksÐ1.5-2.0 L, with side arm.

6.5.8 Pressure filtration apparatusÐMillipore YT30 142 HW, or equivalent.

6.6 Centrifuge Apparatus

6.6.1 CentrifugeÐCapable of rotating 500 mL centrifuge bottles or 15 mL centrifuge tubes at 5,000 rpm minimum.

6.6.2 Centrifuge bottlesÐ500 mL, with screw-caps, to fit centrifuge.

6.6.3 Centrifuge tubesÐ12-15 mL, with screw-caps, to fit centrifuge.

6.7 Cleanup Apparatus

6.7.1 Automated gel permeation chromatograph (Analytical Biochemical Labs, Inc, Columbia, MO, Model GPC Autoprep 1002, or equivalent).

6.7.1.1 ColumnÐ600-700 mm long x 25 mm ID, packed with 70 g of SX-3 Bio-beads (Bio-Rad Laboratories, Richmond, CA, or equivalent).

6.7.1.2 SyringeÐ10 mL, with Luer fitting.

6.7.1.3 Syringe filter holderÐstainless steel, and glass-fiber or fluoropolymer filters (Gelman 4310, or equivalent).

6.7.1.4 UV detectorsÐ254 nm, preparative or semi-preparativeflow cell (Isco, Inc., Type 6; Schmadzu, 5 mm path length; Beckman-Altex152W, 8 µL micro-prepflow cell, 2 mm path; Pharmacia UV-1,3 mm flow cell; LDC Milton-RoyUV-3,monitor #1203; or equivalent).

6.7.2 Reverse-phasehigh-performanceliquid chromatograph.

6.7.2.1 Column oven and detectorÐPerkin-Elmer Model LC-65T(or equivalent) operated at 0.02 AUFS at 235 nm.

6.7.2.2 InjectorÐRheodyne 7120 (or equivalent) with 50 µL sample loop.

6.7.2.3 ColumnÐTwo 6.2 mm x 250 mm Zorbax-ODScolumns in series (DuPont Instruments Division, Wilmington, DE, or equivalent), operated at 50°C with 2.0 mL/min methanol isocratic effluent.

6.7.2.4 PumpÐAltex 110A (or equivalent).

6.7.3 Pipets

6.7.3.1 Disposable, pasteurÐ150 mm long x 5-mmID (Fisher Scientific 13-678-6A, or equivalent).

6.7.3.2 Disposable, serologicalÐ10 mL (6 mm ID).

6.7.4 Glass chromatographic columns

6.7.4.1 150 mm long x 8-mm ID, (Kontes K-420155, or equivalent) with coarse-glassfrit or glass-woolplug and 250 mL reservoir.

6.7.4.2 200 mm long x 15 mm ID, with coarse-glassfrit or glass-woolplug and 250 mL reservoir.

6.7.4.3 300 mm long x 25 mm ID, with 300 mL reservoir and glass or fluoropolymer stopcock.

6.7.5 Stirring apparatus for batch silica cleanup of tissue extracts.

6.7.5.1 Mechanical stirrerÐCorning Model 320, or equivalent.

6.7.5.2 BottleÐ500-600 mL wide-mouthclear glass.

6.7.6 OvenÐFor baking and storage of adsorbents, capable of maintaining a constant temperature (±5°C) in the range of 105-250°C.

6.8 Concentration Apparatus

6.8.1 Rotary evaporatorÐBuchi/Brinkman-American Scientific No. E5045-10 or equivalent, equipped with a variable temperature water bath.

6.8.1.1 Vacuum source for rotary evaporator equipped with shutoff valve at the evaporator and vacuum gauge.

6.8.1.2 A recirculating water pump and chiller are recommended, as use of tap water for cooling the evaporator wastes large volumes of water and can lead to inconsistent performance as water temperatures and pressures vary.

6.8.1.3 Round-bottom flask—100 mL and 500 mL or larger, with ground-glass fitting compatible with the rotary evaporator.

6.8.2 Kuderna-Danish (K-D) Concentrator

6.8.2.1 Concentrator tube—10 mL, graduated (Kontes K-570050-1025, or equivalent) with calibration verified. Ground-glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

6.8.2.2 Evaporation flask—500 mL (Kontes K-570001-0500 or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012 or equivalent).

6.8.2.3 Snyder column—Three-ball macro (Kontes K-503000-0232 or equivalent).

6.8.2.4 Boiling chips

6.8.2.4.1 Glass or silicon carbide—Approximately 10/40 mesh, extracted with methylene chloride and baked at 450°C for one hour minimum.

6.8.2.4.2 Fluoropolymer (optional)—Extracted with methylene chloride.

6.8.2.5 Water bath—Heated, with concentric ring cover, capable of maintaining a temperature within ±2°C, installed in a fume hood.

6.8.3 Nitrogen blowdown apparatus—Equipped with water bath controlled in the range of 30-60°C (N-Evap, Organomation Associates, Inc., South Berlin, MA, or equivalent), installed in a fume hood.

6.8.4 Sample vials

6.8.4.1 Amber glass—2-5 mL with fluoropolymer-lined screw-cap.

6.8.4.2 Glass—0.3 mL, conical, with fluoropolymer-lined screw or crimp cap.

6.9 Gas Chromatograph—Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specifications in Section 10.

6.9.1 GC column for CDDs/CDFs and for isomer specificity for 2,3,7,8-TCDD—60 ±5 m long x 0.32 ±0.02 mm ID; 0.25 µm 5% phenyl, 94% methyl, 1% vinyl silicone bonded-phase fused-silica capillary column (J&W DB-5, or equivalent).

6.9.2 GC column for isomer specificity for 2,3,7,8-TCDFÐ30 ±5 m long x 0.32 ±0.02 mm ID; 0.25 µm bonded-phase fused-silica capillary column (J&W DB-225, or equivalent).

6.10 Mass SpectrometerÐ28-40 eV electron impact ionization, shall be capable of repetitively selectively monitoring 12 exact m/z's minimum at high resolution (≥10,000) during a period of approximately one second, and shall meet all of the performance specifications in Section 10.

6.11 GC/MS InterfaceÐThe mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams.

6.12 Data SystemÐCapable of collecting, recording, and storing MS data.

7.0 Reagents and Standards

7.1 pH Adjustment and Back-Extraction

7.1.1 Potassium hydroxideÐDissolve 20 g reagent grade KOH in 100 mL reagent water.

7.1.2 Sulfuric acidÐReagent grade (specific gravity 1.84).

7.1.3 Hydrochloric acidÐReagent grade, 6N.

7.1.4 Sodium chlorideÐReagent grade, prepare at 5% (w/v) solution in reagent water.

7.2 Solution Drying and Evaporation

7.2.1 Solution dryingÐSodium sulfate, reagent grade, granular, anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride (20 mL/g), baked at 400°C for one hour minimum, cooled in a dessicator, and stored in a pre-cleaned glass bottle with screw-cap that prevents moisture from entering. If, after heating, the sodium sulfate develops a noticeable grayish cast (due to the presence of carbon in the crystal matrix), that batch of reagent is not suitable for use and should be discarded. Extraction with methylene chloride (as opposed to simple rinsing) and baking at a lower temperature may produce sodium sulfate that is suitable for use.

7.2.2 Tissue dryingÐSodium sulfate, reagent grade, powdered, treated and stored as above.

7.2.3 Prepurified nitrogen.

7.3 Extraction

7.3.1 SolventsÐAcetone, toluene, cyclohexane, hexane, methanol, methylene chloride, and nonane; distilled in glass, pesticide quality, lot-certified to be free of interferences.

7.3.2 White quartz sand, 60/70 meshÐFor Soxhlet/Dean-Stark extraction (Aldrich Chemical, Cat. No. 27-437-9,or equivalent). Bake at 450°C for four hours minimum.

7.4 GPC Calibration SolutionÐPrepare a solution containing 300 mg/mL corn oil, 15 mg/mL bis(2-ethylhexyl)phthalate, 1.4 mg/mL pentachlorophenol, 0.1 mg/mL perylene, and 0.5 mg/mL sulfur.

7.5 Adsorbents for Sample Cleanup

7.5.1 Silica gel

7.5.1.1 Activated silica gelÐ100-200 mesh, Supelco 1-3651(or equivalent), rinsed with methylene chloride, baked at 180°C for a minimum of one hour, cooled in a dessicator, and stored in a precleaned glass bottle with screw-cap that prevents moisture from entering.

7.5.1.2 Acid silica gel (30% w/w)ÐThoroughly mix 44.0 g of concentrated sulfuric acid with 100.0 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-linedscrew-cap.

7.5.1.3 Basic silica gelÐThoroughly mix 30 g of 1N sodium hydroxide with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-linedscrew-cap.

7.5.1.4 Potassium silicate

7.5.1.4.1 Dissolve 56 g of high purity potassium hydroxide (Aldrich, or equivalent) in 300 mL of methanol in a 750-1000mL flat-bottom flask.

7.5.1.4.2 Add 100 g of silica gel and a stirring bar, and stir on a hot plate at 60-70°C for one to two hours.

7.5.1.4.3 Decant the liquid and rinse the potassium silicate twice with 100 mL portions of methanol, followed by a single rinse with 100 mL of methylene chloride.

7.5.1.4.4 Spread the potassium silicate on solvent-rinsedaluminum foil and dry for two to four hours in a hood.

7.5.1.4.5 Activate overnight at 200-250°C.

7.5.2 AluminaÐEither one of two types of alumina, acid or basic, may be used in the cleanup of sample extracts, provided that the laboratory can meet the performance specifications for the recovery of labeled compounds described in Section 9.3. The same type of alumina must be used for all samples, including those used to demonstrate initial precision and recovery (Section 9.2) and ongoing precision and recovery (Section 15.5).

7.5.2.1 Acid aluminaÐSupelco 19996-6C(or equivalent). Activate by heating to 130°C for a minimum of 12 hours.

7.5.2.2 Basic aluminaÐSupelco 19944-6C(or equivalent). Activate by heating to 600°C for a minimum of 24 hours. Alternatively, activate by heating in a tube furnace at 650-700°C under an air flow rate of approximately 400 cc/minute. Do not heat over 700°C, as this can lead to reduced capacity for retaining the analytes. Store at 130°C in a covered flask. Use within five days of baking.

7.5.3 Carbon

7.5.3.1 Carbopak CÐ(Supelco 1-0258,or equivalent).

7.5.3.2 Celite 545Ð(Supelco 2-0199,or equivalent).

7.5.3.3 Thoroughly mix 9.0 g Carbopak C and 41.0 g Celite 545 to produce an 18% w/w mixture. Activate the mixture at 130°C for a minimum of six hours. Store in a dessicator.

7.5.4 Anthropogenic isolation columnÐPack the column in Section 6.7.4.3 from bottom to top with the following:

7.5.4.1 2 g silica gel (Section 7.5.1.1).

7.5.4.2 2 g potassium silicate (Section 7.5.1.4).

7.5.4.3 2 g granular anhydrous sodium sulfate (Section 7.2.1).

7.5.4.4 10 g acid silica gel (Section 7.5.1.2).

7.5.4.5 2 g granular anhydrous sodium sulfate.

7.5.5 Florisil column

7.5.5.1 FlorisilÐ60-100 mesh, Floridin Corp (or equivalent). Soxhlet extract in 500 g portions for 24 hours.

7.5.5.2 Insert a glass wool plug into the tapered end of a graduated serological pipet (Section 6.7.3.2). Pack with 1.5 g (approx 2 mL) of Florisil topped with approx 1 mL of sodium sulfate (Section 7.2.1) and a glass wool plug.

7.5.5.3 Activate in an oven at 130-150°C for a minimum of 24 hours and cool for 30 minutes. Use within 90 minutes of cooling.

7.6 Reference MatricesÐMatrices in which the CDDs/CDFs and interfering compounds are not detected by this method.

7.6.1 Reagent waterÐBottled water purchased locally, or prepared by passage through activated carbon.

7.6.2 High-solids reference matrix—Playground sand or similar material. Prepared by extraction with methylene chloride and/or baking at 450°C for a minimum of four hours.

7.6.3 Paper reference matrix—Glass-fiber filter, Gelman Type A, or equivalent. Cut paper to simulate the surface area of the paper sample being tested.

7.6.4 Tissue reference matrix—Corn or other vegetable oil. May be prepared by extraction with methylene chloride.

7.6.5 Other matrices—This method may be verified on any reference matrix by performing the tests given in Section 9.2. Ideally, the matrix should be free of the CDDs/CDFs, but in no case shall the background level of the CDDs/CDFs in the reference matrix exceed three times the minimum levels in Table 2. If low background levels of the CDDs/CDFs are present in the reference matrix, the spike level of the analytes used in Section 9.2 should be increased to provide a spike-to-background ratio in the range of 1:1 to 5:1 (Reference 15).

7.7 Standard Solutions—Purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at room temperature in screw-capped vials with fluoropolymer-lined caps. A mark is placed on the vial at the level of the solution so that solvent loss by evaporation can be detected. If solvent loss has occurred, the solution should be replaced.

7.8 Stock Solutions

7.8.1 Preparation—Prepare in nonane per the steps below or purchase as dilute solutions (Cambridge Isotope Laboratories (CIL), Woburn, MA, or equivalent). Observe the safety precautions in Section 5, and the recommendation in Section 5.1.2.

7.8.2 Dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 1-2 mg of 2,3,7,8-TCDD to three significant figures in a 10 mL ground-glass-stoppered volumetric flask and fill to the mark with nonane. After the TCDD is completely dissolved, transfer the solution to a clean 15 mL vial with fluoropolymer-lined cap.

7.8.3 Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Reference standards that can be used to determine the accuracy of calibration standards are available from CIL and may be available from other vendors.

7.9 PAR Stock Solution

7.9.1 All CDDs/CDFs—Using the solutions in Section 7.8, prepare the PAR stock solution to contain the CDDs/CDFs at the concentrations shown in Table 3. When diluted, the solution will become the PAR (Section 7.14).

7.9.2 If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, prepare the PAR stock solution to contain these compounds only.

7.10 Labeled-Compound Spiking Solution

7.10.1 All CDDs/CDFs—From stock solutions, or from purchased mixtures, prepare this solution to contain the labeled compounds in nonane at the concentrations shown in Table 3. This solution is diluted with acetone prior to use (Section 7.10.3).

7.10.2 If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, prepare the labeled-compound solution to contain these compounds only. This solution is diluted with acetone prior to use (Section 7.10.3).

7.10.3 Dilute a sufficient volume of the labeled compound solution (Section 7.10.1 or 7.10.2) by a factor of 50 with acetone to prepare a diluted spiking solution. Each sample requires 1.0 mL of the diluted solution, but no more solution should be prepared than can be used in one day.

7.11 Cleanup Standard—Prepare $^{37}Cl_4$-2,3,7,8-TCDD in nonane at the concentration shown in Table 3. The cleanup standard is added to all extracts prior to cleanup to measure the efficiency of the cleanup process.

7.12 Internal Standard(s)

7.12.1 All CDDs/CDFs—Prepare the internal standard solution to contain $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD in nonane at the concentration shown in Table 3.

7.12.2 If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, prepare the internal standard solution to contain $^{13}C_{12}$-1,2,3,4-TCDD only.

7.13 Calibration Standards (CS1 through CS5)—Combine the solutions in Sections 7.9 through 7.12 to produce the five calibration solutions shown in Table 4 in nonane. These solutions permit the relative response (labeled to native) and response factor to be measured as a function of concentration. The CS3 standard is used for calibration verification (VER). If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, combine the solutions appropriate to these compounds.

7.14 Precision and Recovery (PAR) Standard—Used for determination of initial (Section 9.2) and ongoing (Section 15.5) precision and recovery. Dilute 10 µL of the precision and recovery standard (Section 7.9.1 or 7.9.2) to 2.0 mL with acetone for each sample matrix for each sample batch. One mL each are required for the blank and OPR with each matrix in each batch.

7.15 GC Retention Time Window Defining Solution and Isomer Specificity Test Standard—Used to define the beginning and ending retention times for the dioxin and furan isomers and to demonstrate isomer specificity of the GC columns employed for determination of 2,3,7,8-TCDD and 2,3,7,8-TCDF. The standard must contain the compounds listed in Table 5 (CIL EDF-4006, or equivalent), at a minimum. It is not necessary to monitor the window-defining compounds if only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be

determined. In this case, an isomer-specificity test standard containing the most closely eluted isomers listed in Table 5 (CIL EDF-4033,or equivalent) may be used.

7.16 QC Check SampleÐA QC Check Sample should be obtained from a source independent of the calibration standards. Ideally, this check sample would be a certified reference material containing the CDDs/CDFs in known concentrations in a sample matrix similar to the matrix under test.

7.17 Stability of SolutionsÐStandard solutions used for quantitative purposes (Sections 7.9 through 7.15) should be analyzed periodically, and should be assayed against reference standards (Section 7.8.3) before further use.

8.0 Sample Collection, Preservation, Storage, and Holding Times

8.1 Collect samples in amber glass containers following conventional sampling practices (Reference 16). Aqueous samples that flow freely are collected in refrigerated bottles using automatic sampling equipment. Solid samples are collected as grab samples using wide-mouthjars.

8.2 Maintain aqueous samples in the dark at 0-4°C from the time of collection until receipt at the laboratory. If residual chlorine is present in aqueous samples, add 80 mg sodium thiosulfate per liter of water. EPA Methods 330.4 and 330.5 may be used to measure residual chlorine (Reference 17). If sample pH is greater than 9, adjust to pH 7-9with sulfuric acid.

Maintain solid, semi-solid,oily, and mixed-phasesamples in the dark at <4°C from the time of collection until receipt at the laboratory.

Store aqueous samples in the dark at 0-4°C. Store solid, semi-solid,oily, mixed-phase, and tissue samples in the dark at <-10°C.

8.3 Fish and Tissue Samples

8.3.1 Fish may be cleaned, filleted, or processed in other ways in the field, such that the laboratory may expect to receive whole fish, fish fillets, or other tissues for analysis.

8.3.2 Fish collected in the field should be wrapped in aluminum foil, and must be maintained at a temperature less than 4°C from the time of collection until receipt at the laboratory.

8.3.3 Samples must be frozen upon receipt at the laboratory and maintained in the dark at <-10°C until prepared. Maintain unused sample in the dark at <-10°C.

8.4 Holding Times

8.4.1 There are no demonstrated maximum holding times associated with CDDs/CDFs in aqueous, solid, semi-solid,tissues, or other sample matrices. If stored in the dark at 0-4°C and preserved as given above (if required), aqueous samples may be stored for up to one year. Similarly, if stored in the dark at <-10°C, solid, semi-solid,multi-phase,and tissue samples may be stored for up to one year.

8.4.2 Store sample extracts in the dark at <-10°C until analyzed. If stored in the dark at <-10°C, sample extracts may be stored for up to one year.

9.0 Quality Assurance/Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 18). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

If the method is to be applied to sample matrix other than water (e.g., soils, filter cake, compost, tissue) the most appropriate alternate matrix (Sections 7.6.2 through 7.6.5) is substituted for the reagent water matrix (Section 7.6.1) in all performance tests.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, and to allow the analyst to overcome sample matrix interferences, the analyst is permitted certain options to improve separations or lower the costs of measurements. These options include alternate extraction, concentration, cleanup procedures, and changes in columns and detectors. Alternate determinative techniques, such as the substitution of spectroscopic or immuno-assaytechniques, and changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in this method is used, that technique must have a specificity equal to or better than the specificity of the techniques in this method for the analytes of interest.

9.1.2.1 Each time a modification is made to this method, the analyst is required to repeat the procedure in Section 9.2. If the detection limit of the method will be affected by the change, the laboratory is required to demonstrate that the MDL (40 CFR Part 136, Appendix B) is lower than one-thirdthe regulatory compliance level or one-thirdthe ML in this method, whichever is higher. If calibration will be affected by the change, the analyst must recalibrate the instrument per Section 10.

9.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and of the quality control officer who witnessed and will verify the analyses and modifications.

9.1.2.2.2 A listing of pollutant(s) measured, by name and CAS Registry number.

9.1.2.2.3 A narrative stating reason(s) for the modifications.

9.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this method, including:

a) Calibration (Section 10.5 through 10.7).
b) Calibration verification (Section 15.3).
c) Initial precision and recovery (Section 9.2).
d) Labeled compound recovery (Section 9.3).
e) Analysis of blanks (Section 9.5).
f) Accuracy assessment (Section 9.4).

9.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

a) Sample numbers and other identifiers.
b) Extraction dates.
c) Analysis dates and times.
d) Analysis sequence/run chronology.
e) Sample weight or volume (Section 11).
f) Extract volume prior to each cleanup step (Section 13).
g) Extract volume after each cleanup step (Section 13).
h) Final extract volume prior to injection (Section 14).
l) Injection volume (Section 14.3).
j) Dilution data, differentiating between dilution of a sample or extract (Section 17.5).
k) Instrument and operating conditions.
l) Column (dimensions, liquid phase, solid support, film thickness, etc).
m) Operating conditions (temperatures, temperature program, flow rates).
n) Detector (type, operating conditions, etc).
o) Chromatograms, printer tapes, and other recordings of raw data.
p) Quantitation reports, data system outputs, and other data to link the raw data to the results reported.

9.1.3 Analyses of method blanks are required to demonstrate freedom from contamination (Section 4.3). The procedures and criteria for analysis of a method blank are described in Sections 9.5 and 15.6.

9.1.4 The laboratory shall spike all samples with labeled compounds to monitor method performance. This test is described in Section 9.3. When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits. Procedures for dilution are given in Section 17.5.

9.1.5 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and the analysis of the ongoing precision and recovery aliquot that

the analytical system is in control. These procedures are described in Sections 15.1 through 15.5.

9.1.6 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in Section 9.4.

9.2 Initial Precision and Recovery (IPR)ÐTo establish the ability to generate acceptable precision and recovery, the analyst shall perform the following operations.

9.2.1 For low solids (aqueous) samples, extract, concentrate, and analyze four 1 L aliquots of reagent water spiked with the diluted labeled compound spiking solution (Section 7.10.3) and the precision and recovery standard (Section 7.14) according to the procedures in Sections 11 through 18. For an alternative sample matrix, four aliquots of the alternative reference matrix (Section 7.6) are used. All sample processing steps that are to be used for processing samples, including preparation (Section 11), extraction (Section 12), and cleanup (Section 13), shall be included in this test.

9.2.2 Using results of the set of four analyses, compute the average concentration (X) of the extracts in ng/mL and the standard deviation of the concentration (s) in ng/mL for each compound, by isotope dilution for CDDs/CDFs with a labeled analog, and by internal standard for 1,2,3,7,8,9-HxCDD,OCDF, and the labeled compounds.

9.2.3 For each CDD/CDF and labeled compound, compare s and X with the corresponding limits for initial precision and recovery in Table 6. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, compare s and X with the corresponding limits for initial precision and recovery in Table 6a. If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test (Section 9.2).

9.3 The laboratory shall spike all samples with the diluted labeled compound spiking solution (Section 7.10.3) to assess method performance on the sample matrix.

9.3.1 Analyze each sample according to the procedures in Sections 11 through 18.

9.3.2 Compute the percent recovery of the labeled compounds and the cleanup standard using the internal standard method (Section 17.2).

9.3.3 The recovery of each labeled compound must be within the limits in Table 7 when all 2,3,7,8-substituted CDDs/CDFs are determined, and within the limits in Table 7a when only 2,3,7,8-TCDD and 2,3,7,8-TCDF are determined. If the recovery of any compound falls outside of these limits, method performance is unacceptable for that compound in that sample. To overcome such difficulties, water samples are diluted and smaller amounts of soils, sludges, sediments, and other matrices are reanalyzed per Section 18.4.

9.4 Recovery of labeled compounds from samples should be assessed and records should be maintained.

9.4.1 After the analysis of five samples of a given matrix type (water, soil, sludge, pulp, etc.) for which the labeled compounds pass the tests in Section 9.3, compute the average percent recovery (R) and the standard deviation of the percent recovery (S_R) for the labeled compounds only. Express the assessment as a percent recovery interval from $R-2S_R$ to $R+2S_R$ for each matrix. For example, if R = 90% and S_R = 10% for five analyses of pulp, the recovery interval is expressed as 70-110%.

9.4.2 Update the accuracy assessment for each labeled compound in each matrix on a regular basis (e.g., after each 5-10 new measurements).

9.5 Method BlanksÐReference matrix method blanks are analyzed to demonstrate freedom from contamination (Section 4.3).

9.5.1 Prepare, extract, clean up, and concentrate a method blank with each sample batch (samples of the same matrix started through the extraction process on the same 12-hour shift, to a maximum of 20 samples). The matrix for the method blank shall be similar to sample matrix for the batch, e.g., a 1 L reagent water blank (Section 7.6.1), high-solids reference matrix blank (Section 7.6.2), paper matrix blank (Section 7.6.3); tissue blank (Section 7.6.4) or alternative reference matrix blank (Section 7.6.5). Analyze the blank immediately after analysis of the OPR (Section 15.5) to demonstrate freedom from contamination.

9.5.2 If any 2,3,7,8-substituted CDD/CDF (Table 1) is found in the blank at greater than the minimum level (Table 2) or one-third the regulatory compliance level, whichever is greater; or if any potentially interfering compound is found in the blank at the minimum level for each level of chlorination given in Table 2 (assuming a response factor of 1 relative to the $^{13}C_{12}$-1,2,3,4-TCDD internal standard for compounds not listed in Table 1), analysis of samples is halted until the blank associated with the sample batch shows no evidence of contamination at this level. All samples must be associated with an uncontaminated method blank before the results for those samples may be reported for regulatory compliance purposes.

9.6 QC Check SampleÐAnalyze the QC Check Sample (Section 7.16) periodically to assure the accuracy of calibration standards and the overall reliability of the analytical process. It is suggested that the QC Check Sample be analyzed at least quarterly.

9.7 The specifications contained in this method can be met if the apparatus used is calibrated properly and then maintained in a calibrated state. The standards used for calibration (Section 10), calibration verification (Section 15.3), and for initial (Section 9.2) and ongoing (Section 15.5) precision and recovery should be identical, so that the most precise results will be obtained. A GC/MS instrument will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of CDDs/CDFs by this method.

9.8 Depending on specific program requirements, field replicates may be collected to determine the precision of the sampling technique, and spiked samples may be required to determine the accuracy of the analysis when the internal standard method is used.

10.0 Calibration

10.1 Establish the operating conditions necessary to meet the minimum retention times for the internal standards in Section 10.2.4 and the relative retention times for the CDDs/CDFs in Table 2.

10.1.1 Suggested GC operating conditions:

Injector temperature:	270°C
Interface temperature:	290°C
Initial temperature:	200°C
Initial time:	Two minutes
Temperature program:	200-220°C, at 5°C/minute
	220°C for 16 minutes
	220-235°C, at 5°C/minute
	235°C for seven minutes
	235-330°C, at 5°C/minute

NOTE: *All portions of the column that connect the GC to the ion source shall remain at or above the interface temperature specified above during analysis to preclude condensation of less volatile compounds.*

Optimize GC conditions for compound separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, IPR and OPR aliquots, and samples.

10.1.2 Mass spectrometer (MS) resolution—Obtain a selected ion current profile (SICP) of each analyte in Table 3 at the two exact m/z's specified in Table 8 and at ≥10,000 resolving power by injecting an authentic standard of the CDDs/CDFs either singly or as part of a mixture in which there is no interference between closely eluted components.

10.1.2.1 The analysis time for CDDs/CDFs may exceed the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass-drift correction is mandatory and a lock-mass m/z from PFK is used for drift correction. The lock-mass m/z is dependent on the exact m/z's monitored within each descriptor, as shown in Table 8. The level of PFK metered into the HRMS during analyses should be adjusted so that the amplitude of the most intense selected lock-mass m/z signal (regardless of the descriptor number) does not exceed 10% of the full-scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

NOTE: *Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source necessitating increased frequency of source cleaning.*

10.1.2.2 If the HRMS has the capability to monitor resolution during the analysis, it is acceptable to terminate the analysis when the resolution falls below 10,000 to save reanalysis time.

10.1.2.3 Using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10% valley) at m/z 304.9824 (PFK) or any other reference signal close to m/z 304 (from TCDF). For each descriptor (Table 8), monitor and record the resolution and exact m/z's of three to five reference peaks covering the mass range of the descriptor. The resolution must be greater than or equal to 10,000, and the deviation between the exact m/z and the theoretical m/z (Table 8) for each exact m/z monitored must be less than 5 ppm.

10.2 Ion Abundance Ratios, Minimum Levels, Signal-to-Noise Ratios, and Absolute Retention Times—Choose an injection volume of either 1 µL or 2 µL, consistent with the capability of the HRGC/HRMS instrument. Inject a 1 µL or 2 µL aliquot of the CS1 calibration solution (Table 4) using the GC conditions from Section 10.1.1. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, the operating conditions and specifications below apply to analysis of those compounds only.

10.2.1 Measure the SICP areas for each analyte, and compute the ion abundance ratios at the exact m/z's specified in Table 8. Compare the computed ratio to the theoretical ratio given in Table 9.

10.2.1.1 The exact m/z's to be monitored in each descriptor are shown in Table 8. Each group or descriptor shall be monitored in succession as a function of GC retention time to ensure that all CDDs/CDFs are detected. Additional m/z's may be monitored in each descriptor, and the m/z's may be divided among more than the five descriptors listed in Table 8, provided that the laboratory is able to monitor the m/z's of all the CDDs/CDFs that may elute from the GC in a given retention-time window. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, the descriptors may be modified to include only the exact m/z's for the tetra- and penta-isomers, the diphenyl ethers, and the lock m/z's.

10.2.1.2 The mass spectrometer shall be operated in a mass-drift correction mode, using perfluorokerosene (PFK) to provide lock m/z's. The lock-mass for each group of m/z's is shown in Table 8. Each lock mass shall be monitored and shall not vary by more than ±20% throughout its respective retention time window. Variations of the lock mass by more than 20% indicate the presence of coeluting interferences that may significantly reduce the sensitivity of the mass spectrometer. Reinjection of another aliquot of the sample extract will not resolve the problem. Additional cleanup of the extract may be required to remove the interferences.

10.2.2 All CDDs/CDFs and labeled compounds in the CS1 standard shall be within the QC limits in Table 9 for their respective ion abundance ratios; otherwise, the mass spectrometer shall be adjusted and this test repeated until the m/z ratios fall within the limits specified. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 10.1.2) prior to repeat of the test.

10.2.3 Verify that the HRGC/HRMS instrument meets the minimum levels in Table 2. The peaks representing the CDDs/CDFs and labeled compounds in the CS1 calibration standard must have signal-to-noise ratios (S/N) greater than or equal to 10.0. Otherwise, the mass spectrometer shall be adjusted and this test repeated until the minimum levels in Table 2 are met.

10.2.4 The absolute retention time of $^{13}C_{12}$-1,2,3,4-TCDD (Section 7.12) shall exceed 25.0 minutes on the DB-5 column, and the retention time of $^{13}C_{12}$-1,2,3,4-TCDD shall exceed 15.0 minutes on the DB-225 column; otherwise, the GC temperature program shall be adjusted and this test repeated until the above-stated minimum retention time criteria are met.

10.3 Retention-Time Windows—Analyze the window defining mixtures (Section 7.15) using the optimized temperature program in Section 10.1. Table 5 gives the elution order (first/last) of the window-defining compounds. If 2,3,7,8-TCDD and 2,3,7,8-TCDF only are to be analyzed, this test is not required.

10.4 Isomer Specificity

10.4.1 Analyze the isomer specificity test standards (Section 7.15) using the procedure in Section 14 and the optimized conditions for sample analysis (Section 10.1.1).

10.4.2 Compute the percent valley between the GC peaks that elute most closely to the 2,3,7,8-TCDD and TCDF isomers, on their respective columns, per Figures 6 and 7.

10.4.3 Verify that the height of the valley between the most closely eluted isomers and the 2,3,7,8-substituted isomers is less than 25% (computed as 100 x/y in Figures 6 and 7). If the valley exceeds 25%, adjust the analytical conditions and repeat the test or replace the GC column and recalibrate (Sections 10.1.2 through 10.7).

10.5 Calibration by Isotope Dilution—Isotope dilution calibration is used for the 15 2,3,7,8-substituted CDDs/CDFs for which labeled compounds are added to samples prior to extraction. The reference compound for each CDD/CDF compound is shown in Table 2.

10.5.1 A calibration curve encompassing the concentration range is prepared for each compound to be determined. The relative response (RR) (labeled to native) vs. concentration in standard solutions is plotted or computed using a linear regression. Relative response is determined according to the procedures described below. Five calibration points are employed.

10.5.2 The response of each CDD/CDF relative to its labeled analog is determined using the area responses of both the primary and secondary exact m/z's specified in Table 8, for each calibration standard, as follows:

$$RR = \frac{(A1_n + A2_n)\ C_l}{(A1_l + A2_l)\ C_n}$$

where,

$A1_n$ and $A2_n$ = The areas of the primary and secondary m/z's for the CDD/CDF.

$A1_l$ and $A2_l$ = The areas of the primary and secondary m/z's for the labeled compound.

C_l = The concentration of the labeled compound in the calibration standard (Table 4).

C_n = The concentration of the native compound in the calibration standard (Table 4).

10.5.3 To calibrate the analytical system by isotope dilution, inject a volume of calibration standards CS1 through CS5 (Section 7.13 and Table 4) identical to the volume chosen in Section 10.2, using the procedure in Section 14 and the conditions in Section 10.1.1 and Table 2. Compute the relative response (RR) at each concentration.

10.5.4 LinearityÐIf the relative response for any compound is constant (less than 20% coefficient of variation) over the five-pointcalibration range, an averaged relative response may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the five-pointcalibration range.

10.6 Calibration by Internal StandardÐThe internal standard method is applied to determination of 1,2,3,7,8,9-HxCDD (Section 17.1.2), OCDF (Section 17.1.1), the non-2,3,7,8-substituted compounds, and to the determination of labeled compounds for intralaboratory statistics (Sections 9.4 and 15.5.4).

10.6.1 Response factorsÐCalibration requires the determination of response factors (RF) defined by the following equation:

$$RF = \frac{(A1_s + A2_s)\ C_{is}}{(A1_{is} + A2_{is})\ C_s}$$

where,

$A1_s$ and $A2_s$ = The areas of the primary and secondary m/z's for the CDD/CDF.

$A1_{is}$ and $A2_{is}$ = The areas of the primary and secondary m/z's for the internal standard

C_{is} = The concentration of the internal standard (Table 4).

C_s = The concentration of the compound in the calibration standard (Table 4).

NOTE: *There is only one m/z for $^{37}Cl_4$-2,3,7,8-TCDD. See Table 8.*

10.6.2 To calibrate the analytical system by internal standard, inject 1.0 µL or 2.0 µL of calibration standards CS1 through CS5 (Section 7.13 and Table 4) using the procedure in Section 14 and the conditions in Section 10.1.1 and Table 2. Compute the response factor (RF) at each concentration.

10.6.3 LinearityÐIf the response factor (RF) for any compound is constant (less than 35% coefficient of variation) over the five-point calibration range, an averaged response factor may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the five-point range.

10.7 Combined CalibrationÐBy using calibration solutions (Section 7.13 and Table 4) containing the CDDs/CDFs and labeled compounds and the internal standards, a single set of analyses can be used to produce calibration curves for the isotope dilution and internal standard methods. These curves are verified each shift (Section 15.3) by analyzing the calibration verification standard (VER, Table 4). Recalibration is required if any of the calibration verification criteria (Section 15.3) cannot be met.

10.8 Data StorageÐMS data shall be collected, recorded, and stored.

10.8.1 Data acquisitionÐThe signal at each exact m/z shall be collected repetitively throughout the monitoring period and stored on a mass storage device.

10.8.2 Response factors and multipoint calibrationsÐThe data system shall be used to record and maintain lists of response factors (response ratios for isotope dilution) and multipoint calibration curves. Computations of relative standard deviation (coefficient of variation) shall be used to test calibration linearity. Statistics on initial performance (Section 9.2) and ongoing performance (Section 15.5) should be computed and maintained, either on the instrument data system, or on a separate computer system.

11.0 Sample Preparation

11.1 Sample preparation involves modifying the physical form of the sample so that the CDDs/CDFs can be extracted efficiently. In general, the samples must be in a liquid form or in the form of finely divided solids in order for efficient extraction to take place. Table 10 lists the phases and suggested quantities for extraction of various sample matrices.

For samples known or expected to contain high levels of the CDDs/CDFs, the smallest sample size representative of the entire sample should be used (see Section 17.5).

For all samples, the blank and IPR/OPR aliquots must be processed through the same steps as the sample to check for contamination and losses in the preparation processes.

11.1.1 For samples that contain particles, percent solids and particle size are determined using the procedures in Sections 11.2 and 11.3, respectively.

11.1.2 Aqueous samplesÐBecause CDDs/CDFs may be bound to suspended particles, the preparation of aqueous samples is dependent on the solids content of the sample.

11.1.2.1 Aqueous samples visibly absent particles are prepared per Section 11.4 and extracted directly using the separatory funnel or SPE techniques in Sections 12.1 or 12.2, respectively.

11.1.2.2 Aqueous samples containing visible particles and containing one percent suspended solids or less are prepared using the procedure in Section 11.4. After preparation, the sample is extracted directly using the SPE technique in 12.2 or filtered per Section 11.4.3. After filtration, the particles and filter are extracted using the SDS procedure in Section 12.3 and the filtrate is extracted using the separatory funnel procedure in Section 12.1.

11.1.2.3 For aqueous samples containing greater than one percent solids, a sample aliquot sufficient to provide 10 g of dry solids is used, as described in Section 11.5.

11.1.3 Solid samples are prepared using the procedure described in Section 11.5 followed by extraction via the SDS procedure in Section 12.3.

11.1.4 Multiphase samplesÐThe phase(s) containing the CDDs/CDFs is separated from the non-CDD/CDF phase using pressure filtration and centrifugation, as described in Section 11.6. The CDDs/CDFs will be in the organic phase in a multiphase sample in which an organic phase exists.

11.1.5 Procedures for grinding, homogenization, and blending of various sample phases are given in Section 11.7.

11.1.6 Tissue samplesÐPreparation procedures for fish and other tissues are given in Section 11.8.

11.2 Determination of Percent Suspended Solids

NOTE: *This aliquot is used for determining the solids content of the sample, not for determination of CDDs/CDFs.*

11.2.1 Aqueous liquids and multi-phasesamples consisting of mainly an aqueous phase.

11.2.1.1 Dessicate and weigh a GF/D filter (Section 6.5.3) to three significant figures.

11.2.1.2 Filter 10.0 ±0.02 mL of well-mixedsample through the filter.

11.2.1.3 Dry the filter a minimum of 12 hours at 110 ±5°C and cool in a dessicator.

11.2.1.4 Calculate percent solids as follows:

$$\%solids = \frac{weight\ of\ sample\ aliquot\ after\ drying\ (g) - weight\ of\ filter\ (g)}{10\ g} \times 100$$

11.2.2 Non-aqueous liquids, solids, semi-solid samples, and multi-phase samples in which the main phase is not aqueous; but not tissues.

11.2.2.1 Weigh 5-10 g of sample to three significant figures in a tared beaker.

11.2.2.2 Dry a minimum of 12 hours at 110 ±5°C, and cool in a dessicator.

11.2.2.3 Calculate percent solids as follows:

$$\%\ solids = \frac{weight\ of\ sample\ aliquot\ after\ drying}{weight\ of\ sample\ aliquot\ before\ drying} \times 100$$

11.3 Determination of Particle Size

11.3.1 Spread the dried sample from Section 11.2.2.2 on a piece of filter paper or aluminum foil in a fume hood or glove box.

11.3.2 Estimate the size of the particles in the sample. If the size of the largest particles is greater than 1 mm, the particle size must be reduced to 1 mm or less prior to extraction using the procedures in Section 11.7.

11.4 Preparation of Aqueous Samples Containing 1% Suspended Solids or Less

11.4.1 Aqueous samples visibly absent particles are prepared per the procedure below and extracted directly using the separatory funnel or SPE techniques in Sections 12.1 or 12.2, respectively. Aqueous samples containing visible particles and one percent suspended solids or less are prepared using the procedure below and extracted using either the SPE technique in Section 12.2 or further prepared using the filtration procedure in Section 11.4.3. The filtration procedure is followed by SDS extraction of the filter and particles (Section 12.3) and separatory funnel extraction of the filtrate (Section 12.1). The SPE procedure is followed by SDS extraction of the filter and disk.

11.4.2 Preparation of sample and QC aliquots

11.4.2.1 Mark the original level of the sample on the sample bottle for reference. Weigh the sample plus bottle to ±1 g.

11.4.2.2 Spike 1.0 mL of the diluted labeled-compound spiking solution (Section 7.10.3) into the sample bottle. Cap the bottle and mix the sample by careful shaking. Allow the sample to equilibrate for one to two hours, with occasional shaking.

11.4.2.3 For each sample or sample batch (to a maximum of 20 samples) to be extracted during the same 12-hour shift, place two 1.0 L aliquots of reagent water in clean sample bottles or flasks.

11.4.2.4 Spike 1.0 mL of the diluted labeled-compound spiking solution (Section 7.10.3) into both reagent water aliquots. One of these aliquots will serve as the method blank.

11.4.2.5 Spike 1.0 mL of the PAR standard (Section 7.14) into the remaining reagent water aliquot. This aliquot will serve as the OPR (Section 15.5).

11.4.2.6 If SPE is to be used, add 5 mL of methanol to the sample, cap and shake the sample to mix thoroughly, and proceed to Section 12.2 for extraction. If SPE is not to be used, and the sample is visibly absent particles, proceed to Section 12.1 for extraction. If SPE is not to be used and the sample contains visible particles, proceed to the following section for filtration of particles.

11.4.3 Filtration of particles

11.4.3.1 Assemble a Buchner funnel (Section 6.5.5) on top of a clean filtration flask. Apply vacuum to the flask, and pour the entire contents of the sample bottle through a glass-fiber filter (Section 6.5.6) in the Buchner funnel, swirling the sample remaining in the bottle to suspend any particles.

11.4.3.2 Rinse the sample bottle twice with approximately 5 mL portions of reagent water to transfer any remaining particles onto the filter.

11.4.3.3 Rinse any particles off the sides of the Buchner funnel with small quantities of reagent water.

11.4.3.4 Weigh the empty sample bottle to ±1 g. Determine the weight of the sample by difference. Save the bottle for further use.

11.4.3.5 Extract the filtrate using the separatory funnel procedure in Section 12.1.

11.4.3.6 Extract the filter containing the particles using the SDS procedure in Section 12.3.

11.5 Preparation of Samples Containing Greater Than 1% Solids

11.5.1 Weigh a well-mixedaliquot of each sample (of the same matrix type) sufficient to provide 10 g of dry solids (based on the solids determination in Section 11.2) into a clean beaker or glass jar.

11.5.2 Spike 1.0 mL of the diluted labeled compound spiking solution (Section 7.10.3) into the sample.

11.5.3 For each sample or sample batch (to a maximum of 20 samples) to be extracted during the same 12-hour shift, weigh two 10 g aliquots of the appropriate reference matrix (Section 7.6) into clean beakers or glass jars.

11.5.4 Spike 1.0 mL of the diluted labeled compound spiking solution (Section 7.10.3) into each reference matrix aliquot. One aliquot will serve as the method blank. Spike 1.0 mL of the PAR standard (Section 7.14) into the other reference matrix aliquot. This aliquot will serve as the OPR (Section 15.5).

11.5.5 Stir or tumble and equilibrate the aliquots for one to two hours.

11.5.6 Decant excess water. If necessary to remove water, filter the sample through a glass-fiberfilter and discard the aqueous liquid.

11.5.7 If particles >1mm are present in the sample (as determined in Section 11.3.2), spread the sample on clean aluminum foil in a hood. After the sample is dry, grind to reduce the particle size (Section 11.7).

11.5.8 Extract the sample and QC aliquots using the SDS procedure in Section 12.3.

11.6 Multiphase Samples

11.6.1 Using the percent solids determined in Section 11.2.1 or 11.2.2, determine the volume of sample that will provide 10 g of solids, up to 1 L of sample.

11.6.2 Pressure filter the amount of sample determined in Section 11.6.1 through Whatman GF/D glass-fiberfilter paper (Section 6.5.3). Pressure filter the blank and OPR aliquots through GF/D papers also. If necessary to separate the phases and/or settle the solids, centrifuge these aliquots prior to filtration.

11.6.3 Discard any aqueous phase (if present). Remove any non-aqueousliquid present and reserve the maximum amount filtered from the sample (Section 11.6.1) or 10 g, whichever is less, for combination with the solid phase (Section 12.3.5).

11.6.4 If particles >1mm are present in the sample (as determined in Section 11.3.2) and the sample is capable of being dried, spread the sample and QC aliquots on clean aluminum foil in a hood. After the aliquots are dry or if the sample cannot be dried, reduce the particle size using the procedures in Section 11.7 and extract the reduced particles using the SDS procedure in Section 12.3. If particles >1mm are not present, extract the particles and filter in the sample and QC aliquots directly using the SDS procedure in Section 12.3.

11.7 Sample grinding, homogenization, or blendingÐSamples with particle sizes greater than 1 mm (as determined in Section 11.3.2) are subjected to grinding, homogenization, or blending. The method of reducing particle size to less than 1 mm is matrix-dependent. In general, hard particles can be reduced by grinding with a mortar and pestle. Softer particles can be reduced by grinding in a Wiley mill or meat grinder, by homogenization, or in a blender.

11.7.1 Each size-reducing preparation procedure on each matrix shall be verified by running the tests in Section 9.2 before the procedure is employed routinely.

11.7.2 The grinding, homogenization, or blending procedures shall be carried out in a glove box or fume hood to prevent particles from contaminating the work environment.

11.7.3 GrindingÐCertain papers and pulps, slurries, and amorphous solids can be ground in a Wiley mill or heavy duty meat grinder. In some cases, reducing the temperature of the sample to freezing or to dry ice or liquid nitrogen temperatures can aid in the grinding process. Grind the sample aliquots from Section 11.5.7 or 11.6.4 in a clean grinder. Do not allow the sample temperature

to exceed 50°C. Grind the blank and reference matrix aliquots using a clean grinder.

11.7.4 Homogenization or blendingÐParticles that are not ground effectively, or particles greater than 1 mm in size after grinding, can often be reduced in size by high speed homogenization or blending. Homogenize and/or blend the particles or filter from Section 11.5.7 or 11.6.4 for the sample, blank, and OPR aliquots.

11.7.5 Extract the aliquots using the SDS procedure in Section 12.3.

11.8 Fish and Other TissuesÐPrior to processing tissue samples, the laboratory must determine the exact tissue to be analyzed. Common requests for analysis of fish tissue include whole fish±skin on, whole fish±skin removed, edible fish fillets (filleted in the field or by the laboratory), specific organs, and other portions. Once the appropriate tissue has been determined, the sample must be homogenized.

11.8.1 Homogenization

11.8.1.1 Samples are homogenized while still frozen, where practical. If the laboratory must dissect the whole fish to obtain the appropriate tissue for analysis, the unused tissues may be rapidly refrozen and stored in a clean glass jar for subsequent use.

11.8.1.2 Each analysis requires 10 g of tissue (wet weight). Therefore, the laboratory should homogenize at least 20 g of tissue to allow for re-extractionof a second aliquot of the same homogenized sample, if re-analysisis required. When whole fish analysis is necessary, the entire fish is homogenized.

11.8.1.3 Homogenize the sample in a tissue homogenizer (Section 6.3.3) or grind in a meat grinder (Section 6.3.4). Cut tissue too large to feed into the grinder into smaller pieces. To assure homogeneity, grind three times.

11.8.1.4 Transfer approximately 10 g (wet weight) of homogenized tissue to a clean, tared, 400-500 mL beaker. For the alternate HCl digestion/extraction, transfer the tissue to a clean, tared 500-600mL wide-mouthbottle. Record the weight to the nearest 10 mg.

11.8.1.5 Transfer the remaining homogenized tissue to a clean jar with a fluoropolymer-linedlid. Seal the jar and store the tissue at <-10°C. Return any tissue that was not homogenized to its original container and store at <-10°C.

11.8.2 QC aliquots

11.8.2.1 Prepare a method blank by adding approximately 10 g of the oily liquid reference matrix (Section 7.6.4) to a 400-500mL beaker. For the alternate HCl digestion/extraction, add the reference matrix to a 500-600mL wide-mouthbottle. Record the weight to the nearest 10 mg.

11.8.2.2 Prepare a precision and recovery aliquot by adding approximately 10 g of the oily liquid reference matrix (Section 7.6.4) to a separate 400-500 mL beaker or wide-mouth bottle, depending on the extraction procedure to be used. Record the weight to the nearest 10 mg. If the initial precision and recovery test is to be performed, use four aliquots; if the ongoing precision and recovery test is to be performed, use a single aliquot.

11.8.3 Spiking

11.8.3.1 Spike 1.0 mL of the labeled compound spiking solution (Section 7.10.3) into the sample, blank, and OPR aliquot.

11.8.3.2 Spike 1.0 mL of the PAR standard (Section 7.14) into the OPR aliquot.

11.8.4 Extract the aliquots using the procedures in Section 12.4.

12.0 Extraction and Concentration

Extraction procedures include separatory funnel (Section 12.1) and solid phase (Section 12.2) for aqueous liquids; Soxhlet/Dean-Stark(Section 12.3) for solids, filters, and SPE disks; and Soxhlet extraction (Section 12.4.1) and HCl digestion (Section 12.4.2) for tissues. Acid/base back-extraction(Section 12.5) is used for initial cleanup of extracts.

Macro-concentration procedures include rotary evaporation (Section 12.6.1), heating mantle (Section 12.6.2), and Kuderna-Danish(K-D)evaporation (Section 12.6.3). Micro-concentration uses nitrogen blowdown (Section 12.7).

12.1 Separatory funnel extraction of filtrates and of aqueous samples visibly absent particles.

12.1.1 Pour the spiked sample (Section 11.4.2.2) or filtrate (Section 11.4.3.5) into a 2 L separatory funnel. Rinse the bottle or flask twice with 5 mL of reagent water and add these rinses to the separatory funnel.

12.1.2 Add 60 mL methylene chloride to the empty sample bottle (Section 12.1.1), seal, and shake 60 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting. Allow the organic layer to separate from the aqueous phase for a minimum of 10 minutes. If an emulsion forms and is more than one-third the volume of the solvent layer, employ mechanical techniques to complete the phase separation (see note below). Drain the methylene chloride extract through a solvent-rinsed glass funnel approximately one-half full of granular

anhydrous sodium sulfate (Section 7.2.1) supported on clean glass-fiberpaper into a solvent-rinsedconcentration device (Section 12.6).

NOTE: *If an emulsion forms, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, use of phase separation paper, centrifugation, use of an ultrasonic bath with ice, addition of NaCl, or other physical methods. Alternatively, solid-phaseor other extraction techniques may be used to prevent emulsion formation. Any alternative technique is acceptable so long as the requirements in Section 9 are met.*

Experience with aqueous samples high in dissolved organic materials (e.g., paper mill effluents) has shown that acidification of the sample prior to extraction may reduce the formation of emulsions. Paper industry methods suggest that the addition of up to 400 mL of ethanol to a 1 L effluent sample may also reduce emulsion formation. However, studies by EPA suggest that the effect may be a result of sample dilution, and that the addition of reagent water may serve the same function. Mechanical techniques may still be necessary to complete the phase separation. If either acidification or addition of ethanol is utilized, the laboratory must perform the startup tests described in Section 9.2 using the same techniques.

12.1.3 Extract the water sample two more times with 60 mL portions of methylene chloride. Drain each portion through the sodium sulfate into the concentrator. After the third extraction, rinse the separatory funnel with at least 20 mL of methylene chloride, and drain this rinse through the sodium sulfate into the concentrator. Repeat this rinse at least twice. Set aside the funnel with sodium sulfate if the extract is to be combined with the extract from the particles.

12.1.4 Concentrate the extract using one of the macro-concentration procedures in Section 12.6.

12.1.4.1 If the extract is from a sample visibly absent particles (Section 11.1.2.1), adjust the final volume of the concentrated extract to approximately 10 mL with hexane, transfer to a 250 mL separatory funnel, and back-extractusing the procedure in Section 12.5.

12.1.4.2 If the extract is from the aqueous filtrate (Section 11.4.3.5), set aside the concentration apparatus for addition of the SDS extract from the particles (Section 12.3.9.1.2).

12.2 SPE of Samples Containing Less Than 1% Solids (References 19-20)

12.2.1 Disk preparation

12.2.1.1 Place an SPE disk on the base of the filter holder (Figure 4) and wet with toluene. While holding a GMF 150 filter above the SPE disk with tweezers, wet the filter with toluene and lay the filter on the SPE disk, making sure that air is not trapped between the filter and disk. Clamp the filter and SPE disk between the 1 L glass reservoir and the vacuum filtration flask.

12.2.1.2 Rinse the sides of the filtration flask with approx 15 mL of toluene using a squeeze bottle or syringe. Apply vacuum momentarily until a few drops appear at the drip tip. Release the vacuum and allow the filter/disk to soak for approx one minute. Apply vacuum and draw all of the toluene through the filter/disk. Repeat the wash step with approx 15 mL of acetone and allow the filter/disk to air dry.

12.2.1.3 Re-wet the filter/disk with approximately 15 mL of methanol, allowing the filter/disk to soak for approximately one minute. Pull the methanol through the filter/disk using the vacuum, but retain a layer of methanol approximately 1 mm thick on the filter. Do not allow the disk to go dry from this point until the end of the extraction.

12.2.1.4 Rinse the filter/disk with two 50-mL portions of reagent water by adding the water to the reservoir and pulling most through, leaving a layer of water on the surface of the filter.

12.2.2 Extraction

12.2.2.1 Pour the spiked sample (Section 11.4.2.2), blank (Section 11.4.2.4), or IPR/OPR aliquot (Section 11.4.2.5) into the reservoir and turn on the vacuum to begin the extraction. Adjust the vacuum to complete the extraction in no less than 10 minutes. For samples containing a high concentration of particles (suspended solids), filtration times may be eight hours or longer.

12.2.2.2 Before all of the sample has been pulled through the filter/disk, rinse the sample bottle with approximately 50 mL of reagent water to remove any solids, and pour into the reservoir. Pull through the filter/disk. Use additional reagent water rinses until all visible solids are removed.

12.2.2.3 Before all of the sample and rinses have been pulled through the filter/disk, rinse the sides of the reservoir with small portions of reagent water.

12.2.2.4 Allow the filter/disk to dry, then remove the filter and disk and place in a glass Petri dish. Extract the filter and disk per Section 12.3.

12.3 SDS Extraction of Samples Containing Particles, and of Filters and/or Disks

12.3.1 Charge a clean extraction thimble (Section 6.4.2.2) with 5.0 g of 100/200 mesh silica (Section 7.5.1.1) topped with 100 g of quartz sand (Section 7.3.2).

NOTE: *Do not disturb the silica layer throughout the extraction process.*

12.3.2 Place the thimble in a clean extractor. Place 30-40 mL of toluene in the receiver and 200-250 mL of toluene in the flask.

12.3.3 Pre-extract the glassware by heating the flask until the toluene is boiling. When properly adjusted, one to two drops of toluene will fall per second from the condenser tip into the receiver. Extract the apparatus for a minimum of three hours.

12.3.4 After pre-extraction, cool and disassemble the apparatus. Rinse the thimble with toluene and allow to air dry.

12.3.5 Load the wet sample, filter, and/or disk from Section 11.4.3.6, 11.5.8, 11.6.4, 11.7.3, 11.7.4, or 12.2.2.4 and any nonaqueous liquid from Section 11.6.3 into the thimble and manually mix into the sand layer with a clean metal spatula, carefully breaking up any large lumps of sample.

12.3.6 Reassemble the pre-extracted SDS apparatus, and add a fresh charge of toluene to the receiver and reflux flask. Apply power to the heating mantle to begin refluxing. Adjust the reflux rate to match the rate of percolation through the sand and silica beds until water removal lessens the restriction to toluene flow. Frequently check the apparatus for foaming during the first two hours of extraction. If foaming occurs, reduce the reflux rate until foaming subsides.

12.3.7 Drain the water from the receiver at one to two hours and eight to nine hours, or sooner if the receiver fills with water. Reflux the sample for a total of 16-24 hours. Cool and disassemble the apparatus. Record the total volume of water collected.

12.3.8 Remove the distilling flask. Drain the water from the Dean-Stark receiver and add any toluene in the receiver to the extract in the flask.

12.3.9 Concentrate the extract using one of the macro-concentration procedures in Section 12.6 per the following:

12.3.9.1 Extracts from the particles in an aqueous sample containing less than 1% solids (Section 11.4.3.6).

12.3.9.1.1 Concentrate the extract to approximately 5 mL using the rotary evaporator or heating mantle procedures in Section 12.6.1 or 12.6.2.

12.3.9.1.2 Quantitatively transfer the extract through the sodium sulfate (Section 12.1.3) into the apparatus that was set aside (Section 12.1.4.2) and reconcentrate to the level of the toluene.

12.3.9.1.3 Adjust to approximately 10 mL with hexane, transfer to a 250 mL separatory funnel, and proceed with back-extraction (Section 12.5).

12.3.9.2 Extracts from particles (Sections 11.5 through 11.6) or from the SPE filter and disk (Section 12.2.2.4)ÐConcentrate to approximately 10 mL using the rotary evaporator or heating mantle (Section 12.6.1

or 12.6.2), transfer to a 250 mL separatory funnel, and proceed with back-extraction (Section 12.5).

12.4 Extraction of TissueÐTwo procedures are provided for tissue extraction.

12.4.1 Soxhlet extraction (Reference 21)

12.4.1.1 Add 30-40g of powdered anhydrous sodium sulfate to each of the beakers (Section 11.8.4) and mix thoroughly. Cover the beakers with aluminum foil and allow to equilibrate for 12-24 hours. Remix prior to extraction to prevent clumping.

12.4.1.2 Assemble and pre-extractthe Soxhlet apparatus per Sections 12.3.1 through 12.3.4, except use the methylene chloride:hexane (1:1) mixture for the pre-extraction and rinsing and omit the quartz sand. The Dean-Stark moisture trap may also be omitted, if desired.

12.4.1.3 Reassemble the pre-extracted Soxhlet apparatus and add a fresh charge of methylene chloride:hexane to the reflux flask.

12.4.1.4 Transfer the sample/sodium sulfate mixture (Section 12.4.1.1) to the Soxhlet thimble, and install the thimble in the Soxhlet apparatus.

12.4.1.5 Rinse the beaker with several portions of solvent mixture and add to the thimble. Fill the thimble/receiver with solvent. Extract for 18-24 hours.

12.4.1.6 After extraction, cool and disassemble the apparatus.

12.4.1.7 Quantitatively transfer the extract to a macro-concentrationdevice (Section 12.6), and concentrate to near dryness. Set aside the concentration apparatus for re-use.

12.4.1.8 Complete the removal of the solvent using the nitrogen blowdown procedure (Section 12.7) and a water bath temperature of 60°C. Weigh the receiver, record the weight, and return the receiver to the blowdown apparatus, concentrating the residue until a constant weight is obtained.

12.4.1.9 Percent lipid determinationÐThe lipid content is determined by extraction of tissue with the same solvent system (methylene chloride:hexane) that was used in EPA@s National Dioxin Study (Reference 22) so that lipid contents are consistent with that study.

12.4.1.9.1 Redissolve the residue in the receiver in hexane and spike 1.0 mL of the cleanup standard (Section 7.11) into the solution.

12.4.1.9.2 Transfer the residue/hexane to the anthropogenic isolation column (Section 13.7.1) or bottle for the acidified silica gel batch cleanup (Section 13.7.2), retaining the boiling chips in the concentration apparatus. Use several rinses to assure that all material is transferred. If necessary, sonicate or heat the receiver slightly to assure that all material is re-dissolved. Allow the receiver to dry. Weigh the receiver and boiling chips.

12.4.1.9.3 Calculate the lipid content to the nearest three significant figures as follows:

$$\textit{Percent lipid} = \frac{\textit{Weight of residue (g)}}{\textit{Weight of tissue (g)}} \times 100$$

12.4.1.9.4 It is not necessary to determine the lipid content of the blank, IPR, or OPR aliquots.

12.4.2 HCl digestion/extraction and concentration (References 23-26)

12.4.2.1 Add 200 mL of 6 N HCl and 200 mL of methylene chloride:hexane (1:1) to the sample and QC aliquots (Section 11.8.4).

12.4.2.2 Cap and shake each bottle one to three times. Loosen the cap in a hood to vent excess pressure. Shake each bottle for 10-30seconds and vent.

12.4.2.3 Tightly cap and place on shaker. Adjust the shaker action and speed so that the acid, solvent, and tissue are in constant motion. However, take care to avoid such violent action that the bottle may be dislodged from the shaker. Shake for 12-24hours.

12.4.2.4 After digestion, remove the bottles from the shaker. Allow the bottles to stand so that the solvent and acid layers separate.

12.4.2.5 Decant the solvent through a glass funnel with glass-fiber filter (Sections 6.5.2 through 6.5.3) containing approximately 10 g of granular anhydrous sodium sulfate (Section 7.2.1) into a macro-concentration apparatus (Section 12.6). Rinse the contents of the bottle with two 25 mL portions of hexane and pour through the sodium sulfate into the apparatus.

12.4.2.6 Concentrate the solvent to near dryness using a macro-concentration procedure (Section 12.6).

12.4.2.7 Complete the removal of the solvent using the nitrogen blowdown apparatus (Section 12.7) and a water bath temperature of 60°C. Weigh the receiver, record the weight, and return the receiver to the blowdown apparatus, concentrating the residue until a constant weight is obtained.

12.4.2.8 Percent lipid determination—The lipid content is determined in the same solvent system [methylene chloride:hexane (1:1)] that was used in EPA's National Dioxin Study (Reference 22) so that lipid contents are consistent with that study.

12.4.2.8.1 Redissolve the residue in the receiver in hexane and spike 1.0 mL of the cleanup standard (Section 7.11) into the solution.

12.4.2.8.2 Transfer the residue/hexane to the narrow-mouth 100-200mL bottle retaining the boiling chips in the receiver. Use several rinses to assure that all material is transferred, to a maximum hexane volume of approximately 70 mL. Allow the receiver to dry. Weigh the receiver and boiling chips.

12.4.2.8.3 Calculate the percent lipid per Section 12.4.1.9.3. It is not necessary to determine the lipid content of the blank, IPR, or OPR aliquots.

12.4.2.9 Clean up the extract per Section 13.7.3.

12.5 Back-Extraction with Base and Acid

12.5.1 Spike 1.0 mL of the cleanup standard (Section 7.11) into the separatory funnels containing the sample and QC extracts from Section 12.1.4.1, 12.3.9.1.3, or 12.3.9.2.

12.5.2 Partition the extract against 50 mL of potassium hydroxide solution (Section 7.1.1). Shake for two minutes with periodic venting into a hood. Remove and discard the aqueous layer. Repeat the base washing until no color is visible in the aqueous layer, to a maximum of four washings. Minimize contact time between the extract and the base to prevent degradation of the CDDs/CDFs. Stronger potassium hydroxide solutions may be employed for back-extraction, provided that the laboratory meets the specifications for labeled compound recovery and demonstrates acceptable performance using the procedure in Section 9.2.

12.5.3 Partition the extract against 50 mL of sodium chloride solution (Section 7.1.4) in the same way as with base. Discard the aqueous layer.

12.5.4 Partition the extract against 50 mL of sulfuric acid (Section 7.1.2) in the same way as with base. Repeat the acid washing until no color is visible in the aqueous layer, to a maximum of four washings.

12.5.5 Repeat the partitioning against sodium chloride solution and discard the aqueous layer.

12.5.6 Pour each extract through a drying column containing 7-10 cm of granular anhydrous sodium sulfate (Section 7.2.1). Rinse the separatory funnel with 30-50mL of solvent, and pour through the drying column. Collect each extract in a round-bottomflask. Re-concentratethe sample and QC aliquots per Sections 12.6 through 12.7, and clean up the samples and QC aliquots per Section 13.

12.6 Macro-ConcentrationÐExtracts in toluene are concentrated using a rotary evaporator or a heating mantle; extracts in methylene chloride or hexane are concentrated using a rotary evaporator, heating mantle, or Kuderna-Danishapparatus.

12.6.1 Rotary evaporationÐConcentrate the extracts in separate round-bottomflasks.

12.6.1.1 Assemble the rotary evaporator according to manufacturer's instructions, and warm the water bath to 45°C. On a daily basis, preclean the rotary evaporator by concentrating 100 mL of clean extraction solvent through the system. Archive both the concentrated solvent and the solvent in the catch flask for a contamination check if necessary. Between samples, three 2-3mL aliquots of solvent should be rinsed down the feed tube into a waste beaker.

12.6.1.2 Attach the round-bottomflask containing the sample extract to the rotary evaporator. Slowly apply vacuum to the system, and begin rotating the sample flask.

12.6.1.3 Lower the flask into the water bath, and adjust the speed of rotation and the temperature as required to complete concentration in 15-20minutes. At the proper rate of concentration, the flow of solvent into the receiving flask will be steady, but no bumping or visible boiling of the extract will occur.

NOTE: *If the rate of concentration is too fast, analyte loss may occur.*

12.6.1.4 When the liquid in the concentration flask has reached an apparent volume of approximately 2 mL, remove the flask from the water bath and stop the rotation. Slowly and carefully admit air into the system. Be sure not to open the valve so quickly that the sample is blown out of the flask. Rinse the feed tube with approximately 2 mL of solvent.

12.6.1.5 Proceed to Section 12.6.4 for preparation for back-extraction or micro-concentrationand solvent exchange.

12.6.2 Heating mantleÐConcentrate the extracts in separate round-bottomflasks.

12.6.2.1 Add one or two clean boiling chips to the round-bottomflask, and attach a three-ballmacro Snyder column. Prewet the column by adding approximately 1 mL of solvent through the top. Place the round-bottomflask in a heating mantle, and apply heat as required to complete the concentration in 15-20minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.

12.6.2.2 When the liquid has reached an apparent volume of approximately 10 mL, remove the round-bottomflask from the heating mantle and allow the solvent to drain and cool for at least 10 minutes.

Remove the Snyder column and rinse the glass joint into the receiver with small portions of solvent.

12.6.2.3 Proceed to Section 12.6.4 for preparation for back-extraction or micro-concentrationand solvent exchange.

12.6.3 Kuderna-Danish(K-D)ÐConcentrate the extracts in separate 500 mL K-Dflasks equipped with 10 mL concentrator tubes. The K-Dtechnique is used for solvents such as methylene chloride and hexane. Toluene is difficult to concentrate using the K-Dtechnique unless a water bath fed by a steam generator is used.

12.6.3.1 Add one to two clean boiling chips to the receiver. Attach a three-ball macro Snyder column. Prewet the column by adding approximately 1 mL of solvent through the top. Place the K-D apparatus in a hot water bath so that the entire lower rounded surface of the flask is bathed with steam.

12.6.3.2 Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

12.6.3.3 When the liquid has reached an apparent volume of 1 mL, remove the K-Dapparatus from the bath and allow the solvent to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of solvent. A 5 mL syringe is recommended for this operation.

12.6.3.4 Remove the three-ballSnyder column, add a fresh boiling chip, and attach a two-ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of solvent through the top. Place the apparatus in the hot water bath.

12.6.3.5 Adjust the vertical position and the water temperature as required to complete the concentration in 5-10minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

12.6.3.6 When the liquid reaches an apparent volume of 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes.

12.6.3.7 Proceed to 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.

12.6.4 Preparation for back-extractionor micro-concentrationand solvent exchange.

12.6.4.1 For back-extraction(Section 12.5), transfer the extract to a 250 mL separatory funnel. Rinse the concentration vessel with small

portions of hexane, adjust the hexane volume in the separatory funnel to 10-20mL, and proceed to back-extraction(Section 12.5).

12.6.4.2 For determination of the weight of residue in the extract, or for clean-upprocedures other than back-extraction,transfer the extract to a blowdown vial using two to three rinses of solvent. Proceed with micro-concentrationand solvent exchange (Section 12.7).

12.7 Micro-Concentrationand Solvent Exchange

12.7.1 Extracts to be subjected to GPC or HPLC cleanup are exchanged into methylene chloride. Extracts to be cleaned up using silica gel, alumina, carbon, and/or Florisil are exchanged into hexane.

12.7.2 Transfer the vial containing the sample extract to a nitrogen blowdown device. Adjust the flow of nitrogen so that the surface of the solvent is just visibly disturbed.

NOTE: *A large vortex in the solvent may cause analyte loss.*

12.7.3 Lower the vial into a 45°C water bath and continue concentrating.

12.7.3.1 If the extract is to be concentrated to dryness for weight determination (Sections 12.4.1.8, 12.4.2.7, and 13.7.1.4), blow dry until a constant weight is obtained.

12.7.3.2 If the extract is to be concentrated for injection into the GC/MS or the solvent is to be exchanged for extract cleanup, proceed as follows:

12.7.4 When the volume of the liquid is approximately 100 µL, add 2-3 mL of the desired solvent (methylene chloride for GPC and HPLC, or hexane for the other cleanups) and continue concentration to approximately 100 µL. Repeat the addition of solvent and concentrate once more.

12.7.5 If the extract is to be cleaned up by GPC, adjust the volume of the extract to 5.0 mL with methylene chloride. If the extract is to be cleaned up by HPLC, further concentrate the extract to 30 µL. Proceed with GPC or HPLC cleanup (Section 13.2 or 13.6, respectively).

12.7.6 If the extract is to be cleaned up by column chromatography (alumina, silica gel, Carbopak/Celite, or Florisil), bring the final volume to 1.0 mL with hexane. Proceed with column cleanups (Sections 13.3 through 13.5 and 13.8).

12.7.7 If the extract is to be concentrated for injection into the GC/MS (Section 14), quantitatively transfer the extract to a 0.3 mL conical vial for final concentration, rinsing the larger vial with hexane and adding the rinse to the conical vial. Reduce the volume to approximately 100 µL. Add 10 µL of nonane to the vial, and evaporate the solvent to the level of the nonane. Seal the vial and label with the sample number. Store in the dark at room temperature until ready for

GC/MS analysis. If GC/MS analysis will not be performed on the same day, store the vial at <-10°C.

13.0 Extract Cleanup

13.1 Cleanup may not be necessary for relatively clean samples (e.g., treated effluents, groundwater, drinking water). If particular circumstances require the use of a cleanup procedure, the analyst may use any or all of the procedures below or any other appropriate procedure. Before using a cleanup procedure, the analyst must demonstrate that the requirements of Section 9.2 can be met using the cleanup procedure. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, the cleanup procedures may be optimized for isolation of these two compounds.

13.1.1 Gel permeation chromatography (Section 13.2) removes high molecular weight interferences that cause GC column performance to degrade. It should be used for all soil and sediment extracts and may be used for water extracts that are expected to contain high molecular weight organic compounds (e.g., polymeric materials, humic acids).

13.1.2 Acid, neutral, and basic silica gel (Section 13.3), alumina (Section 13.4), and Florisil (Section 13.8) are used to remove nonpolar and polar interferences. Alumina and Florisil are used to remove chlorodiphenyl ethers.

13.1.3 Carbopak/Celite (Section 13.5) is used to remove nonpolar interferences.

13.1.4 HPLC (Section 13.6) is used to provide specificity for the 2,3,7,8-substituted and other CDD and CDF isomers.

13.1.5 The anthropogenic isolation column (Section 13.7.1), acidified silica gel batch adsorption procedure (Section 13.7.2), and sulfuric acid and base back-extraction (Section 13.7.3) are used for removal of lipids from tissue samples.

13.2 Gel Permeation Chromatography (GPC)

13.2.1 Column packing

13.2.1.1 Place 70-75g of SX-3 Bio-beads (Section 6.7.1.1) in a 400-500mL beaker.

13.2.1.2 Cover the beads with methylene chloride and allow to swell overnight (a minimum of 12 hours).

13.2.1.3 Transfer the swelled beads to the column (Section 6.7.1.1) and pump solvent through the column, from bottom to top, at 4.5-5.5mL/minute prior to connecting the column to the detector.

13.2.1.4 After purging the column with solvent for one to two hours, adjust the column head pressure to 7-10psig and purge for four to five hours to remove air. Maintain a head pressure of 7-10 psig. Connect the column to the detector (Section 6.7.1.4).

13.2.2 Column calibration

13.2.2.1 Load 5 mL of the calibration solution (Section 7.4) into the sample loop.

13.2.2.2 Inject the calibration solution and record the signal from the detector. The elution pattern will be corn oil, bis(2-ethyl hexyl)phthalate, pentachlorophenol, perylene, and sulfur.

13.2.2.3 Set the "dump time" to allow >85% removal of the corn oil and >85% collection of the phthalate.

13.2.2.4 Set the "collect time" to the peak minimum between perylene and sulfur.

13.2.2.5 Verify the calibration with the calibration solution after every 20 extracts. Calibration is verified if the recovery of the pentachlorophenol is greater than 85%. If calibration is not verified, the system shall be recalibrated using the calibration solution, and the previous 20 samples shall be re-extracted and cleaned up using the calibrated GPC system.

13.2.3 Extract cleanupÐGPC requires that the column not be overloaded. The column specified in this method is designed to handle a maximum of 0.5 g of high molecular weight material in a 5 mL extract. If the extract is known or expected to contain more than 0.5 g, the extract is split into aliquots for GPC, and the aliquots are combined after elution from the column. The residue content of the extract may be obtained gravimetrically by evaporating the solvent from a 50 µL aliquot.

13.2.3.1 Filter the extract or load through the filter holder (Section 6.7.1.3) to remove the particles. Load the 5.0 mL extract onto the column.

13.2.3.2 Elute the extract using the calibration data determined in Section 13.2.2. Collect the eluate in a clean 400-500mL beaker.

13.2.3.3 Rinse the sample loading tube thoroughly with methylene chloride between extracts to prepare for the next sample.

13.2.3.4 If a particularly dirty extract is encountered, a 5.0 mL methylene chloride blank shall be run through the system to check for carry-over.

13.2.3.5 Concentrate the eluate per Sections 12.6 and 12.7 for further cleanup or injection into the GC/MS.

13.3 Silica Gel Cleanup

13.3.1 Place a glass-woolplug in a 15 mm ID chromatography column (Section 6.7.4.2). Pack the column bottom to top with: 1 g silica gel (Section 7.5.1.1), 4 g basic silica gel (Section 7.5.1.3), 1 g silica gel, 8 g acid silica gel (Section 7.5.1.2), 2 g silica gel,

and 4 g granular anhydrous sodium sulfate (Section 7.2.1). Tap the column to settle the adsorbents.

13.3.2 Pre-elute the column with 50-100 mL of hexane. Close the stopcock when the hexane is within 1 mm of the sodium sulfate. Discard the eluate. Check the column for channeling. If channeling is present, discard the column and prepare another.

13.3.3 Apply the concentrated extract to the column. Open the stopcock until the extract is within 1 mm of the sodium sulfate.

13.3.4 Rinse the receiver twice with 1 mL portions of hexane, and apply separately to the column. Elute the CDDs/CDFs with 100 mL hexane, and collect the eluate.

13.3.5 Concentrate the eluate per Sections 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.

13.3.6 For extracts of samples known to contain large quantities of other organic compounds (such as paper mill effluents), it may be advisable to increase the capacity of the silica gel column. This may be accomplished by increasing the strengths of the acid and basic silica gels. The acid silica gel (Section 7.5.1.2) may be increased in strength to as much as 44% w/w (7.9 g sulfuric acid added to 10 g silica gel). The basic silica gel (Section 7.5.1.3) may be increased in strength to as much as 33% w/w (50 mL 1N NaOH added to 100 g silica gel), or the potassium silicate (Section 7.5.1.4) may be used.

NOTE: *The use of stronger acid silica gel (44% w/w) may lead to charring of organic compounds in some extracts. The charred material may retain some of the analytes and lead to lower recoveries of CDDs/CDFs. Increasing the strengths of the acid and basic silica gel may also require different volumes of hexane than those specified above to elute the analytes off the column. Therefore, the performance of the method after such modifications must be verified by the procedure in Section 9.2.*

13.4 Alumina Cleanup

13.4.1 Place a glass-wool plug in a 15 mm ID chromatography column (Section 6.7.4.2).

13.4.2 If using acid alumina, pack the column by adding 6 g acid alumina (Section 7.5.2.1). If using basic alumina, substitute 6 g basic alumina (Section 7.5.2.2). Tap the column to settle the adsorbents.

13.4.3 Pre-elute the column with 50-100 mL of hexane. Close the stopcock when the hexane is within 1 mm of the alumina.

13.4.4 Discard the eluate. Check the column for channeling. If channeling is present, discard the column and prepare another.

13.4.5 Apply the concentrated extract to the column. Open the stopcock until the extract is within 1 mm of the alumina.

13.4.6 Rinse the receiver twice with 1 mL portions of hexane and apply separately to the column. Elute the interfering compounds with 100 mL hexane and discard the eluate.

13.4.7 The choice of eluting solvents will depend on the choice of alumina (acid or basic) made in Section 13.4.2.

13.4.7.1 If using acid alumina, elute the CDDs/CDFs from the column with 20 mL methylene chloride:hexane (20:80 v/v). Collect the eluate.

13.4.7.2 If using basic alumina, elute the CDDs/CDFs from the column with 20 mL methylene chloride:hexane (50:50 v/v). Collect the eluate.

13.4.8 Concentrate the eluate per Sections 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.

13.5 Carbon Column

13.5.1 Cut both ends from a 10 mL disposable serological pipet (Section 6.7.3.2) to produce a 10 cm column. Fire-polish both ends and flare both ends if desired. Insert a glass-wool plug at one end, and pack the column with 0.55 g of Carbopak/Celite (Section 7.5.3.3) to form an adsorbent bed approximately 2 cm long. Insert a glass-wool plug on top of the bed to hold the adsorbent in place.

13.5.2 Pre-elute the column with 5 mL of toluene followed by 2 mL of methylene chloride: methanol:toluene (15:4:1 v/v), 1 mL of methylene chloride:cyclohexane (1:1 v/v), and 5 mL of hexane. If the flow rate of eluate exceeds 0.5 mL/minute, discard the column.

13.5.3 When the solvent is within 1 mm of the column packing, apply the sample extract to the column. Rinse the sample container twice with 1 mL portions of hexane and apply separately to the column. Apply 2 mL of hexane to complete the transfer.

13.5.4 Elute the interfering compounds with two 3 mL portions of hexane, 2 mL of methylene chloride:cyclohexane (1:1 v/v), and 2 mL of methylene chloride:methanol:toluene (15:4:1 v/v). Discard the eluate.

13.5.5 Invert the column, and elute the CDDs/CDFs with 20 mL of toluene. If carbon particles are present in the eluate, filter through glass-fiber filter paper.

13.5.6 Concentrate the eluate per Sections 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.

13.6 HPLC (Reference 6)

13.6.1 Column calibration

13.6.1.1 Prepare a calibration standard containing the 2,3,7,8-substituted isomers and/or other isomers of interest at a concentration of approximately 500 pg/µL in methylene chloride.

13.6.1.2 Inject 30 µL of the calibration solution into the HPLC and record the signal from the detector. Collect the eluant for reuse. The elution order will be the tetra- through octa-isomers.

13.6.1.3 Establish the collection time for the tetra-isomersand for the other isomers of interest. Following calibration, flush the injection system with copious quantities of methylene chloride, including a minimum of five 50 µL injections while the detector is monitored, to ensure that residual CDDs/CDFs are removed from the system.

13.6.1.4 Verify the calibration with the calibration solution after every 20 extracts. Calibration is verified if the recovery of the CDDs/CDFs from the calibration standard (Section 13.6.1.1) is 75-125% compared to the calibration (Section 13.6.1.2). If calibration is not verified, the system shall be recalibrated using the calibration solution, and the previous 20 samples shall be re-extracted and cleaned up using the calibrated system.

13.6.2 Extract cleanupÐHPLC requires that the column not be overloaded. The column specified in this method is designed to handle a maximum of 30 µL of extract. If the extract cannot be concentrated to less than 30 µL, it is split into fractions and the fractions are combined after elution from the column.

13.6.2.1 Rinse the sides of the vial twice with 30 µL of methylene chloride and reduce to 30 µL with the evaporation apparatus (Section 12.7).

13.6.2.2 Inject the 30 µL extract into the HPLC.

13.6.2.3 Elute the extract using the calibration data determined in Section 13.6.1. Collect the fraction(s) in a clean 20 mL concentrator tube containing 5 mL of hexane:acetone (1:1 v/v).

13.6.2.4 If an extract containing greater than 100 ng/mL of total CDD or CDF is encountered, a 30 µL methylene chloride blank shall be run through the system to check for carry-over.

13.6.2.5 Concentrate the eluate per Section 12.7 for injection into the GC/MS.

13.7 Cleanup of Tissue LipidsÐLipids are removed from the Soxhlet extract using either the anthropogenic isolation column (Section 13.7.1) or acidified silica gel (Section 13.7.2), or are removed from the HCl digested extract using sulfuric acid and base back-extraction (Section 13.7.3).

13.7.1 Anthropogenic isolation column (References 22 and 27)ÐUsed for removal of lipids from the Soxhlet/SDS extraction (Section 12.4.1).

13.7.1.1 Prepare the column as given in Section 7.5.4.

13.7.1.2 Pre-elutethe column with 100 mL of hexane. Drain the hexane layer to the top of the column, but do not expose the sodium sulfate.

13.7.1.3 Load the sample and rinses (Section 12.4.1.9.2) onto the column by draining each portion to the top of the bed. Elute the CDDs/CDFs from the column into the apparatus used for concentration (Section 12.4.1.7) using 200 mL of hexane.

13.7.1.4 Concentrate the cleaned up extract (Sections 12.6 through 12.7) to constant weight per Section 12.7.3.1. If more than 500 mg of material remains, repeat the cleanup using a fresh anthropogenic isolation column.

13.7.1.5 Redissolve the extract in a solvent suitable for the additional cleanups to be used (Sections 13.2 through 13.6 and 13.8).

13.7.1.6 Spike 1.0 mL of the cleanup standard (Section 7.11) into the residue/solvent.

13.7.1.7 Clean up the extract using the procedures in Sections 13.2 through 13.6 and 13.8. Alumina (Section 13.4) or Florisil (Section 13.8) and carbon (Section 13.5) are recommended as minimum additional cleanup steps.

13.7.1.8 Following cleanup, concentrate the extract to 10 µL as described in Section 12.7 and proceed with the analysis in Section 14.

13.7.2 Acidified silica gel (Reference 28)ÐProcedure alternate to the anthropogenic isolation column (Section 13.7.1) that is used for removal of lipids from the Soxhlet/SDS extraction (Section 12.4.1).

13.7.2.1 Adjust the volume of hexane in the bottle (Section 12.4.1.9.2) to approximately 200 mL.

13.7.2.2 Spike 1.0 mL of the cleanup standard (Section 7.11) into the residue/solvent.

13.7.2.3 Drop the stirring bar into the bottle, place the bottle on the stirring plate, and begin stirring.

13.7.2.4 Add 30-100g of acid silica gel (Section 7.5.1.2) to the bottle while stirring, keeping the silica gel in motion. Stir for two to three hours.

NOTE: *30 grams of silica gel should be adequate for most samples and will minimize contamination from this source.*

13.7.2.5 After stirring, pour the extract through approximately 10 g of granular anhydrous sodium sulfate (Section 7.2.1) contained in a funnel with glass-fiberfilter into a macro contration device (Section 12.6). Rinse the bottle and sodium sulfate with hexane to complete the transfer.

13.7.2.6 Concentrate the extract per Sections 12.6 through 12.7 and clean up the extract using the procedures in Sections 13.2 through 13.6 and 13.8. Alumina (Section 13.4) or Florisil (Section 13.8) and carbon (Section 13.5) are recommended as minimum additional cleanup steps.

13.7.3 Sulfuric acid and base back-extractionÐUsed with HCl digested extracts (Section 12.4.2).

13.7.3.1 Spike 1.0 mL of the cleanup standard (Section 7.11) into the residue/solvent (Section 12.4.2.8.2).

13.7.3.2 Add 10 mL of concentrated sulfuric acid to the bottle. Immediately cap and shake one to three times. Loosen cap in a hood to vent excess pressure. Cap and shake the bottle so that the residue/solvent is exposed to the acid for a total time of approximately 45 seconds.

13.7.3.3 Decant the hexane into a 250 mL separatory funnel making sure that no acid is transferred. Complete the quantitative transfer with several hexane rinses.

13.7.3.4 Back extract the solvent/residue with 50 mL of potassium hydroxide solution per Section 12.5.2, followed by two reagent water rinses.

13.7.3.5 Drain the extract through a filter funnel containing approximately 10 g of granular anhydrous sodium sulfate in a glass-fiberfilter into a macro concentration device (Section 12.6).

13.7.3.6 Concentrate the cleaned up extract to a volume suitable for the additional cleanups given in Sections 13.2 through 13.6 and 13.8. Gel permeation chromatography (Section 13.2), alumina (Section 13.4) or Florisil (Section 13.8), and Carbopak/Celite (Section 13.5) are recommended as minimum additional cleanup steps.

13.7.3.7 Following cleanup, concentrate the extract to 10 µL as described in Section 12.7 and proceed with analysis per Section 14.

13.8 Florisil Cleanup (Reference 29)

13.8.1 Pre-elutethe activated Florisil column (Section 7.5.3) with 10 mL of methylene chloride followed by 10 mL of hexane:methylene chloride (98:2 v/v) and discard the solvents.

13.8.2 When the solvent is within 1 mm of the packing, apply the sample extract (in hexane) to the column. Rinse the sample container twice with 1 mL portions of hexane and apply to the column.

13.8.3 Elute the interfering compounds with 20 mL of hexane:methylene chloride (98:2) and discard the eluate.

13.8.4 Elute the CDDs/CDFs with 35 mL of methylene chloride and collect the eluate. Concentrate the eluate per Sections 12.6 through 12.7 for further cleanup or for injection into the HPLC or GC/MS.

14.0 HRGC/HRMS Analysis

14.1 Establish the operating conditions given in Section 10.1.

14.2 Add 10 µL of the appropriate internal standard solution (Section 7.12) to the sample extract immediately prior to injection to minimize the possibility of loss by evaporation, adsorption, or reaction. If an extract is to be reanalyzed and evaporation has occurred, do not add more instrument internal standard solution. Rather, bring the extract back to its previous volume (e.g., 19 µL) with pure nonane only (18 µL if 2 µL injections are used).

14.3 Inject 1.0 µL or 2.0 µL of the concentrated extract containing the internal standard solution, using on-columnor splitless injection. The volume injected must be identical to the volume used for calibration (Section 10). Start the GC column initial isothermal hold upon injection. Start MS data collection after the solvent peak elutes. Stop data collection after the OCDD and OCDF have eluted. If only 2,3,7,8-TCDDand 2,3,7,8-TCDF are to be determined, stop data collection after elution of these compounds. Return the column to the initial temperature for analysis of the next extract or standard.

15.0 System and Laboratory Performance

15.1 At the beginning of each 12-hourshift during which analyses are performed, GC/MS system performance and calibration are verified for all CDDs/CDFs and labeled compounds. For these tests, analysis of the CS3 calibration verification (VER) standard (Section 7.13 and Table 4) and the isomer specificity test standards (Section 7.15 and Table 5) shall be used to verify all performance criteria. Adjustment and/or recalibration (Section 10) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples, blanks, IPRs, and OPRs be analyzed.

15.2 MS ResolutionÐA static resolving power of at least 10,000 (10% valley definition) must be demonstrated at the appropriate m/z before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each 12-hour shift according to procedures in Section 10.1.2. Corrective actions must be implemented whenever the resolving power does not meet the requirement.

15.3 Calibration Verification

15.3.1 Inject the VER standard using the procedure in Section 14.

15.3.2 The m/z abundance ratios for all CDDs/CDFs shall be within the limits in Table 9; otherwise, the mass spectrometer shall be adjusted until the m/z abundance ratios fall within the limits specified, and the verification test shall be repeated. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 10.1.2) prior to repeat of the verification test.

15.3.3 The peaks representing each CDD/CDF and labeled compound in the VER standard must be present with S/N of at least 10; otherwise, the mass spectrometer shall be adjusted and the verification test repeated.

15.3.4 Compute the concentration of each CDD/CDF compound by isotope dilution (Section 10.5) for those compounds that have labeled analogs (Table 1). Compute the concentration of the labeled compounds by the internal standard method (Section 10.6). These concentrations are computed based on the calibration data in Section 10.

15.3.5 For each compound, compare the concentration with the calibration verification limit in Table 6. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, compare the concentration to the limit in Table 6a. If all compounds meet the acceptance criteria, calibration has been verified and analysis of standards and sample extracts may proceed. If, however, any compound fails its respective limit, the measurement system is not performing properly for that compound. In this event, prepare a fresh calibration standard or correct the problem causing the failure and repeat the resolution (Section 15.2) and verification (Section 15.3) tests, or recalibrate (Section 10).

15.4 Retention Times and GC Resolution

15.4.1 Retention times

15.4.1.1 AbsoluteÐThe absolute retention times of the $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD GCMS internal standards in the verification test (Section 15.3) shall be within ±15 seconds of the retention times obtained during calibration (Sections 10.2.1 and 10.2.4).

15.4.1.2 RelativeÐThe relative retention times of CDDs/CDFs and labeled compounds in the verification test (Section 15.3) shall be within the limits given in Table 2.

15.4.2 GC resolution

15.4.2.1 Inject the isomer specificity standards (Section 7.15) on their respective columns.

15.4.2.2 The valley height between 2,3,7,8-TCDD and the other tetra-dioxin isomers at m/z 319.8965, and between 2,3,7,8-TCDF and the other tetra-furan isomers at m/z 303.9016 shall not exceed 25% on their respective columns (Figures 6 and 7).

15.4.3 If the absolute retention time of any compound is not within the limits specified or if the 2,3,7,8-isomersare not resolved, the GC is not performing properly. In this event, adjust the GC and repeat the verification test (Section 15.3) or recalibrate (Section 10), or replace the GC column and either verify calibration or recalibrate.

15.5 Ongoing Precision and Recovery

15.5.1 Analyze the extract of the ongoing precision and recovery (OPR) aliquot (Section 11.4.2.5, 11.5.4, 11.6.2, 11.7.4, or 11.8.3.2) prior to analysis of samples from the same batch.

15.5.2 Compute the concentration of each CDD/CDF by isotope dilution for those compounds that have labeled analogs (Section 10.5). Compute the concentration of 1,2,3,7,8,9-HxCDD,OCDF, and each labeled compound by the internal standard method (Section 10.6).

15.5.3 For each CDD/CDF and labeled compound, compare the concentration to the OPR limits given in Table 6. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, compare the concentration to the limits in Table 6a. If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual concentration falls outside of the range given, the extraction/concentration processes are not being performed properly for that compound. In this event, correct the problem, re-prepare, extract, and clean up the sample batch and repeat the ongoing precision and recovery test (Section 15.5).

15.5.4 Add results that pass the specifications in Section 15.5.3 to initial and previous ongoing data for each compound in each matrix. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each CDD/CDF in each matrix type by calculating the average percent recovery (R) and the standard deviation of percent recovery (S_R). Express the accuracy as a recovery interval from $R-2S_R$ to $R+2S_R$. For example, if R = 95% and S_R = 5%, the accuracy is 85-105%.

15.6 BlankÐAnalyze the method blank extracted with each sample batch immediately following analysis of the OPR aliquot to demonstrate freedom from contamination and freedom from carryover from the OPR analysis. The results of the analysis of the blank must meet the specifications in Section 9.5.2 before sample analyses may proceed.

16.0 Qualitative Determination

A CDD, CDF, or labeled compound is identified in a standard, blank, or sample when all of the criteria in Sections 16.1 through 16.4 are met.

16.1 The signals for the two exact m/z's in Table 8 must be present and must maximize within the same two seconds.

16.2 The signal-to-noiseratio (S/N) for the GC peak at each exact m/z must be greater than or equal to 2.5 for each CDD or CDF detected in a sample extract, and greater than or equal to 10 for all CDDs/CDFs in the calibration standard (Sections 10.2.3 and 15.3.3).

16.3 The ratio of the integrated areas of the two exact m/z's specified in Table 8 must be within the limit in Table 9, or within ±10% of the ratio in the midpoint (CS3) calibration or calibration verification (VER), whichever is most recent.

16.4 The relative retention time of the peak for a 2,3,7,8-substituted CDD or CDF must be within the limit in Table 2. The retention time of peaks representing non-2,3,7,8-substituted CDDs/CDFs must be within the retention time windows established in Section 10.3.

16.5 Confirmatory Analysis—Isomer specificity for 2,3,7,8-TCDF cannot be achieved on the DB-5 column. Therefore, any sample in which 2,3,7,8-TCDF is identified by analysis on a DB-5 column must have a confirmatory analysis performed on a DB-225, SP-2330, or equivalent GC column. The operating conditions in Section 10.1.1 may be adjusted to optimize the analysis on the second GC column, but the GC/MS must meet the mass resolution and calibration specifications in Section 10.

16.6 If the criteria for identification in Sections 16.1 through 16.5 are not met, the CDD or CDF has not been identified and the results may not be reported for regulatory compliance purposes. If interferences preclude identification, a new aliquot of sample must be extracted, further cleaned up, and analyzed.

17.0 Quantitative Determination

17.1 Isotope Dilution Quantitation—By adding a known amount of a labeled compound to every sample prior to extraction, correction for recovery of the CDD/CDF can be made because the CDD/CDF and its labeled analog exhibit similar effects upon extraction, concentration, and gas chromatography. Relative response (RR) values are used in conjunction with the initial calibration data described in Section 10.5 to determine concentrations directly, so long as labeled compound spiking levels are constant, using the following equation:

$$C_{ex}\ (ng/mL) = \frac{(A1_n + A2_n)\ C_l}{(A1_l + A2_l)\ RR}$$

where,

C_{ex} = The concentration of the CDD/CDF in the extract, and the other terms are as defined in Section 10.5.2.

17.1.1 Because of a potential interference, the labeled analog of OCDF is not added to the sample. Therefore, OCDF is quantitated against labeled OCDD. As a result, the concentration of OCDF is corrected for the recovery of the labeled OCDD. In instances where OCDD and OCDF behave differently during sample extraction, concentration, and cleanup procedures, this may decrease the accuracy of the OCDF results. However, given the low toxicity of this compound relative to the other dioxins and furans, the potential decrease in accuracy is not considered significant.

17.1.2 Because $^{13}C_{12}$-1,2,3,7,8,9-HxCDD is used as an instrument internal standard (i.e., not added before extraction of the sample), it cannot be used to quantitate the 1,2,3,7,8,9-HxCDD by strict isotope dilution procedures. Therefore, 1,2,3,7,8,9-HxCDD is quantitated using the averaged response of the labeled analogs of the other two 2,3,7,8-substituted HxCDDs: 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD. As a result, the concentration of 1,2,3,7,8,9-HxCDD is corrected for the average recovery of the other two HxCDDs.

17.1.3 Any peaks representing non-2,3,7,8-substituted CDDs/CDFs are quantitated using an average of the response factors from all of the labeled 2,3,7,8-isomers at the same level of chlorination.

17.2 Internal Standard Quantitation and Labeled Compound Recovery

17.2.1 Compute the concentrations of 1,2,3,7,8,9-HxCDD, OCDF, the ^{13}C-labeled analogs and the ^{37}C-labeled cleanup standard in the extract using the response factors determined from the initial calibration data (Section 10.6) and the following equation:

$$C_{ex}\ (ng/mL) = \frac{(A1_s + A2_s)\ C_{is}}{(A1_{is} + A2_{is})\ RF}$$

where,

C_{ex} = The concentration of the CDD/CDF in the extract, and the other terms are as defined in Section 10.6.1.

NOTE: *There is only one m/z for the ^{37}Cl-labeled standard.*

17.2.2 Using the concentration in the extract determined above, compute the percent recovery of the ^{13}C-labeled compounds and the ^{37}C-labeled cleanup standard using the following equation:

$$\text{Recovery (\%)} = \frac{\text{Concentration found } (\mu g/mL)}{\text{Concentration spiked } (\mu g/mL)} \times 100$$

17.3 The concentration of a CDD/CDF in the solid phase of the sample is computed using the concentration of the compound in the extract and the weight of the solids (Section 11.5.1), as follows:

$$\text{Concentration in solid } (ng/kg) = \frac{(C_{ex} \times V_{ex})}{W_s}$$

where,

C_{ex} = The concentration of the compound in the extract.
V_{ex} = The extract volume in mL.
W_s = The sample weight (dry weight) in kg.

17.4 The concentration of a CDD/CDF in the aqueous phase of the sample is computed using the concentration of the compound in the extract and the volume of water extracted (Section 11.4 or 11.5), as follows:

$$\text{Concentration in aqueous phase (pg/L)} = \frac{(C_{ex} \times V_{ex})}{V_s}$$

where,

C_{ex} = The concentration of the compound in the extract.
V_{ex} = The extract volume in mL.
V_s = The sample volume in liters.

17.5 If the SICP area at either quantitation m/z for any compound exceeds the calibration range of the system, a smaller sample aliquot is extracted.

17.5.1 For aqueous samples containing 1% solids or less, dilute 100 mL, 10 mL, etc., of sample to 1 L with reagent water and re-prepare,extract, clean up, and analyze per Sections 11 through 14.

17.5.2 For samples containing greater than 1% solids, extract an amount of sample equal to 1/10, 1/100, etc., of the amount used in Section 11.5.1. Re-prepare,extract, clean up, and analyze per Sections 11 through 14.

17.5.3 If a smaller sample size will not be representative of the entire sample, dilute the sample extract by a factor of 10, adjust the concentration of the instrument internal standard to 100 pg/µL in the extract, and analyze an aliquot of this diluted extract by the internal standard method.

17.6 Results are reported to three significant figures for the CDDs/CDFs and labeled compounds found in all standards, blanks, and samples.

17.6.1 Reporting units and levels

17.6.1.1 Aqueous samplesÐReport results in pg/L (parts-per-quadrillion).

17.6.1.2 Samples containing greater than 1% solids (soils, sediments, filter cake, compost)ÐReport results in ng/kg based on the dry weight of the sample. Report the percent solids so that the result may be corrected.

17.6.1.3 TissuesÐReport results in ng/kg of wet tissue, not on the basis of the lipid content of the sample. Report the percent lipid content, so that the data user can calculate the concentration on a lipid basis if desired.

17.6.1.4 Reporting level

17.6.1.4.1 Standards (VER, IPR, OPR) and samplesÐReport results at or above the minimum level (Table 2). Report results below the minimum level as not detected or as required by the regulatory authority.

17.6.1.4.2 BlanksÐReport results above one-third the ML.

17.6.2 Results for CDDs/CDFs in samples that have been diluted are reported at the least dilute level at which the areas at the quantitation m/z's are within the calibration range (Section 17.5).

17.6.3 For CDDs/CDFs having a labeled analog, results are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (Section 17.5) and the labeled compound recovery is within the normal range for the method (Section 9.3 and Tables 6, 6a, 7, and 7a).

17.6.4 Additionally, if requested, the total concentration of all isomers in an individual level of chlorination (i.e., total TCDD, total TCDF, total Paced, etc.) may be reported by summing the concentrations of all isomers identified in that level of chlorination, including both 2,3,7,8-substituted and non-2,3,7,8-substituted isomers.

18.0 Analysis of Complex Samples

18.1 Some samples may contain high levels (>10 ng/L; >1000 ng/kg) of the compounds of interest, interfering compounds, and/or polymeric materials. Some extracts will not concentrate to 10 µL (Section 12.7); others may overload the GC column and/or mass spectrometer.

18.2 Analyze a smaller aliquot of the sample (Section 17.5) when the extract will not concentrate to 10 µL after all cleanup procedures have been exhausted.

18.3 Chlorodiphenyl EthersÐIf chromatographic peaks are detected at the retention time of any CDDs/CDFs in any of the m/z channels being monitored for the chlorodiphenyl ethers (Table 8), cleanup procedures must be employed until these interferences are removed. Alumina (Section 13.4) and Florisil (Section 13.8) are recommended for removal of chlorodiphenyl ethers.

18.4 Recovery of Labeled CompoundsÐIn most samples, recoveries of the labeled compounds will be similar to those from reagent water or from the alternate matrix (Section 7.6).

18.4.1 If the recovery of any of the labeled compounds is outside of the normal range (Table 7), a diluted sample shall be analyzed (Section 17.5).

18.4.2 If the recovery of any of the labeled compounds in the diluted sample is outside of normal range, the calibration verification standard (Section 7.13) shall be analyzed and calibration verified (Section 15.3).

18.4.3 If the calibration cannot be verified, a new calibration must be performed and the original sample extract reanalyzed.

18.4.4 If the calibration is verified and the diluted sample does not meet the limits for labeled compound recovery, the method does not apply to the sample being analyzed and the result may not be reported for regulatory compliance purposes. In this case, alternate extraction and cleanup procedures in this method must be employed to resolve the interference. If all cleanup procedures in this method have been employed and labeled compound recovery remains outside of the normal range, extraction and/or cleanup procedures that are beyond this scope of this method will be required to analyze these samples.

19.0 Pollution Prevention

19.1 The solvents used in this method pose little threat to the environment when managed properly. The solvent evaporation techniques used in this method are amenable to solvent recovery, and it is recommended that the laboratory recover solvents wherever feasible.

19.2 Standards should be prepared in volumes consistent with laboratory use to minimize disposal of standards.

20.0 Waste Management

20.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations.

20.2 Samples containing HCl to pH <2 are hazardous and must be neutralized before being poured down a drain or must be handled as hazardous waste.

20.3 The CDDs/CDFs decompose above 800°C. Low-level waste such as absorbent paper, tissues, animal remains, and plastic gloves may be burned in an appropriate incinerator. Gross quantities (milligrams) should be packaged securely and disposed of through commercial or governmental channels that are capable of handling extremely toxic wastes.

20.4 Liquid or soluble waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light with a wavelength shorter than 290 nm for several days. Use F40 BL or equivalent lamps. Analyze liquid wastes, and dispose of the solutions when the CDDs/CDFs can no longer be detected.

20.5 For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel" and "Less is Better±Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

21.0 Method Performance

Method performance was validated and performance specifications were developed using data from EPA's international interlaboratory validation study (References 30-31)and the

EPA / paper industry Long-Term Variability Study of discharges from the pulp and paper industry (58 FR 66078).

22.0 References

1. Tondeur, Yves. "Method 8290: Analytical Procedures and Quality Assurance for Multimedia Analysis of Polychlorinated Dibenzo-*p*-dioxinsand Dibenzofurans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry," USEPA EMSL, Las Vegas, Nevada, June 1987.

2. "Measurement of 2,3,7,8-Tetrachlorinated Dibenzo-*p*-dioxin (TCDD) and 2,3,7,8-Tetrachlorinated Dibenzofuran (TCDF) in Pulp, Sludges, Process Samples and Wastewaters from Pulp and Paper Mills," Wright State University, Dayton, OH 45435, June 1988.

3. "NCASI Procedures for the Preparation and Isomer Specific Analysis of Pulp and Paper Industry Samples for 2,3,7,8-TCDDand 2,3,7,8-TCDF," National Council of the Paper Industry for Air and Stream Improvement Inc., 260 Madison Avenue, New York, NY 10016, Technical Bulletin No. 551, Pre-ReleaseCopy, July 1988.

4. "Analytical Procedures and Quality Assurance Plan for the Determination of PCDD/PCDF in Fish," USEPA, Environmental Research Laboratory, 6201 Congdon Boulevard, Duluth, MN 55804, April 1988.

5. Tondeur, Yves. "Proposed GC/MS Methodology for the Analysis of PCDDs and PCDFs in Special Analytical Services Samples," Triangle Laboratories, Inc., 801-10Capitola Dr, Research Triangle Park, NC 27713, January 1988; updated by personal communication September 1988.

6. Lamparski, L.L. and Nestrick, T.J. "Determination of Tetra-, Hexa-, Hepta-, and Octachlorodibenzo-*p*-dioxinIsomers in Particulate Samples at Parts per Trillion Levels," *Analytical Chemistry*, 52: 2045-2054,1980.

7. Lamparski, L.L. and Nestrick, T.J. "Novel Extraction Device for the Determination of Chlorinated Dibenzo-*p*-dioxins (PCDDs) and Dibenzofurans (PCDFs) in Matrices Containing Water," *Chemosphere*, 19:27-31,1989.

8. Patterson, D.G., et. al. "Control of Interferences in the Analysis of Human Adipose Tissue for 2,3,7,8-Tetrachlorodibenzo*p*-dioxin," *Environmental Toxicological Chemistry*, 5:355-360,1986.

9. Stanley, John S. and Sack, Thomas M. "Protocol for the Analysis of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxinby High Resolution Gas Chromatography/High Resolution Mass Spectrometry," USEPA EMSL, Las Vegas, Nevada 89114, EPA 600/4-86-004, January 1986.

10. "Working with Carcinogens," Department of Health, Education, & Welfare, Public Health Service, Centers for Disease Control, NIOSH, Publication 77-206,August 1977, NTIS PB-277256.

11. "OSHA Safety and Health Standards, General Industry," OSHA 2206, 29 *CFR* 1910.

12. "Safety in Academic Chemistry Laboratories," ACS Committee on Chemical Safety, 1979.

13. "Standard Methods for the Examination of Water and Wastewater," 18th edition and later revisions, American Public Health Association, 1015 15th St, N.W., Washington, DC 20005, 1-35: Section 1090 (Safety), 1992.

14. "Method 613Ð2,3,7,8-Tetrachlorodibenzo-*p*-dioxin," 40 *CFR* 136 (49 *FR* 43234), October 26, 1984, Section 4.1.

15. Provost, L.P. and Elder, R.S. "Interpretation of Percent Recovery Data," *American Laboratory*, 15: 56-83, 1983.

16. "Standard Practice for Sampling Water," ASTM Annual Book of Standards, ASTM, 1916 Race Street, Philadelphia, PA 19103-1187, 1980.

17. "Methods 330.4 and 330.5 for Total Residual Chlorine," USEPA, EMSL, Cincinnati, OH 45268, EPA 600/4-79-020, March 1979.

18. "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," USEPA EMSL, Cincinnati, OH 45268, EPA-600/4-79-019, March 1979.

19. Williams, Rick. Letter to Bill Telliard, June 4, 1993, available from the EPA Sample Control Center operated by DynCorp Viar, Inc., 300 N Lee St, Alexandria, VA 22314, 703-519-1140.

20. Barkowski, Sarah. Fax to Sue Price, August 6, 1992, available from the EPA Sample Control Center operated by DynCorp Viar, Inc., 300 N Lee St, Alexandria VA 22314, 703-519-1140.

21. "Analysis of Multi-media, Multi-concentration Samples for Dioxins and Furans, PCDD/PCDF Analyses Data Package", Narrative for Episode 4419, MRI Project No. 3091-A, op.cit. February 12, 1993, Available from the EPA Sample Control Center operated by DynCorp Viar Inc, 300 N Lee St, Alexandria, VA 22314 (703-519-1140).

22. "Analytical Procedures and Quality Assurance Plan for the Determination of PCDD/PCDF in Fish", U.S. Environmental Protection Agency, Environmental Research Laboratory, Duluth, MN 55804, EPA/600/3-90/022, March 1990.

23. Afghan, B.K., Carron, J., Goulden, P.D., Lawrence, J., Leger, D., Onuska, F., Sherry, J., and Wilkenson, R.J., "Recent Advances in Ultratrace Analysis of Dioxins and Related Halogenated Hydrocarbons", *Can J. Chem.*, 65: 1086-1097, 1987.

24. Sherry, J.P. and Tse, H. "A Procedure for the Determination of Polychlorinated Dibenzo-*p*-dioxinsin Fish", *Chemosphere*, 20: 865-872, 1990.

25. "Preliminary Fish Tissue Study", Results of Episode 4419, available from the EPA Sample Control Center operated by DynCorp Viar, Inc., 300 N Lee St, Alexandria, VA 22314, 703-519-1140.

26. Nestrick, Terry L. DOW Chemical Co., personal communication with D.R. Rushneck, April 8, 1993. Details available from the U.S. Environmental Protection Agency Sample Control Center operated by DynCorp Viar Inc, 300 N Lee St, Alexandria, VA 22314, 703-519-1140.

27. Barnstadt, Michael. "Big Fish Column", Triangle Laboratories of RTP, Inc., SOP 129-90, 27 March 27, 1992.

28. "Determination of Polychlorinated Dibenzo-*p*-Dioxins(PCDD) and Dibenzofurans (PCDF) in Environmental Samples Using EPA Method 1613", Chemical Sciences Department, Midwest Research Institute, 425 Volker Boulevard, Kansas City, MO 44110-2299, Standard Operating Procedure No. CS-153,January 15, 1992.

29. Ryan, John J. Raymonde Lizotte and William H. Newsome, *J. Chromatog.* 303 (1984) 351-360.

30. Telliard, William A., McCarty, Harry B., and Riddick, Lynn S. "Results of the Interlaboratory Validation Study of USEPA Method 1613 for the Analysis of Tetra- through Octachlorinated Dioxins and Furans by Isotope Dilution GC/MS," *Chemosphere*, 27, 41-46(1993).

31. "Results of the International Interlaboratory Validation Study of USEPA Method 1613", October 1994, available from the EPA Sample Control Center operated by DynCorp Viar, Inc., 300 N Lee St, Alexandria, VA 22314, 703-519-1140.

23.0 Tables and Figures

TABLE 1. CHLORINATED DIBENZO-*P*-DIOXINSAND FURANS DETERMINED BY ISOTOPE DILUTION AND INTERNAL STANDARD HIGH RESOLUTION GAS CHROMATOGRAPHY (HRGC)/HIGH RESOLUTION MASS SPECTROMETRY (HRMS)

CDDs/CDFs [1]	CAS Registry	Labeled analog	CAS Registry
2,3,7,8-TCDD	1746-01-6	$^{13}C_{12}$-2,3,7,8-TCDD	76523-40-5
		$^{37}Cl_4$-2,3,7,8-TCDD	85508-50-5
Total TCDD	41903-57-5	Ð	Ð
2,3,7,8-TCDF	51207-31-9	$^{13}C_{12}$-2,3,7,8-TCDF	89059-46-1
Total-TCDF	55722-27-5	Ð	Ð
1,2,3,7,8-PeCDD	40321-76-4	$^{13}C_{12}$-1,2,3,7,8-PeCDD	109719-79-1
Total-PeCDD	36088-22-9	Ð	Ð
1,2,3,7,8-PeCDF	57117-41-6	$^{13}C_{12}$-1,2,3,7,8-PeCDF	109719-77-9
2,3,4,7,8-PeCDF	57117-31-4	$^{13}C_{12}$-2,3,4,7,8-PeCDF	116843-02-8
Total-PeCDF	30402-15-4	Ð	Ð
1,2,3,4,7,8-HxCDD	39227-28-6	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	109719-80-4
1,2,3,6,7,8-HxCDD	57653-85-7	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	109719-81-5
1,2,3,7,8,9-HxCDD	19408-74-3	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	109719-82-6
Total-HxCDD	34465-46-8	Ð	Ð
1,2,3,4,7,8-HxCDF	70648-26-9	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	114423-98-2
1,2,3,6,7,8-HxCDF	57117-44-9	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	116843-03-9
1,2,3,7,8,9-HxCDF	72918-21-9	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	116843-04-0
2,3,4,6,7,8-HxCDF	60851-34-5	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	116843-05-1
Total-HxCDF	55684-94-1	Ð	Ð
1,2,3,4,6,7,8-HpCDD	35822-46-9	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	109719-83-7
Total-HpCDD	37871-00-4	Ð	Ð
1,2,3,4,6,7,8-HpCDF	67562-39-4	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	109719-84-8
1,2,3,4,7,8,9-HpCDF	55673-89-7	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	109719-94-0
Total-HpCDF	38998-75-3	Ð	Ð
OCDD	3268-87-9	$^{13}C_{12}$-OCDD	114423-97-1
OCDF	39001-02-0	not used	Ð

[1] Chlorinated dibenzo-*p*-dioxinsand chlorinated dibenzofurans

TCDD = Tetrachlorodibenzo-*p*-dioxin
PeCDD = Pentachlorodibenzo-*p*-dioxin
HxCDD = Hexachlorodibenzo-*p*-dioxin
HpCDD = Heptachlorodibenzo-*p*-dioxin
OCDD = Octachlorodibenzo-*p*-dioxin

TCDF = Tetrachlorodibenzofuran
PeCDF = Pentachlorodibenzofuran
HxCDF = Hexachlorodibenzofuran
HpCDF = Heptachlorodibenzofuran
OCDF = Octachlorodibenzofuran

TABLE 2. RETENTION TIME REFERENCES, QUANTITATION REFERENCES, RELATIVE RETENTION TIMES, AND MINIMUM LEVELS FOR CDDS AND CDFS

CDD/CDF	Retention time and quantitation reference	Relative retention time	Minimum level[1] Water (pg/L; ppq)	Solid (ng/kg; ppt)	Extract (pg/µL; ppb)
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the injection internal standard					
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	0.999±1.003	10	1	0.5
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	0.999±1.002	10	1	0.5
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF	0.999±1.002	50	5	2.5
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	0.999±1.002	50	5	2.5
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	0.999±1.002	50	5	2.5
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD	0.923±1.103			
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.976±1.043			
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.989±1.052			
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.000±1.425			
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.011±1.526			
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD	1.000±1.567			
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the injection internal standard					
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	0.999±1.001	50	5	2.5
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	0.997±1.005	50	5	2.5
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	0.999±1.001	50	5	2.5
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	0.999±1.001	50	5	2.5
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	0.999±1.001	50	5	2.5
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8,-HxCDD	0.998±1.004	50	5	2.5
1,2,3,7,8,9-HxCDD	Ð[2]	1.000±1.019	50	5	2.5
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	0.999±1.001	50	5	2.5
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	0.999±1.001	50	5	2.5
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	0.999±1.001	50	5	2.5
OCDF	$^{13}C_{12}$-OCDD	0.999±1.008	100	10	5.0
OCDD	$^{13}C_{12}$-OCDD	0.999±1.001	100	10	5.0
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.944±0.970			
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.949±0.975			
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977±1.047			
$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.959±1.021			
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977±1.000			
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.981±1.003			
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.043±1.085			

TABLE 2. RETENTION TIME REFERENCES, QUANTITATION REFERENCES, RELATIVE RETENTION TIMES, AND MINIMUM LEVELS FOR CDDS AND CDFS

CDD/CDF	Retention time and quantitation reference	Relative retention time	Minimum level[1] Water (pg/L; ppq)	Solid (ng/kg; ppt)	Extract (pg/µL; ppb)
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.057±1.151			
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.086±1.110			
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.032±1.311			

[1]The Minimum Level (ML) for each analyte is defined as the level at which the entire analytical system must give a recognizable signal and acceptable calibration point. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

[2]The retention time reference for 1,2,3,7,8,9-HxCDD is $^{13}C_{12}$-1,2,3,6,7,8-HxCDD, and 1,2,3,7,8,9-HxCDD is quantified using the averaged responses for $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD.

TABLE 3. CONCENTRATION OF STOCK AND SPIKING SOLUTIONS CONTAINING CDDS/CDFS AND LABELED COMPOUNDS

CDD/CDF	Labeled Compound Stock Solution [1] (ng/mL)	Labeled Compound Spiking Solution [2] (ng/mL)	PAR Stock Solution [3] (ng/mL)	PAR Spiking Solution [4] (ng/mL)
2,3,7,8-TCDD	Ð	Ð	40	0.8
2,3,7,8-TCDF	Ð	Ð	40	0.8
1,2,3,7,8-PeCDD	Ð	Ð	200	4
1,2,3,7,8-PeCDF	Ð	Ð	200	4
2,3,4,7,8-PeCDF	Ð	Ð	200	4
1,2,3,4,7,8-HxCDD	Ð	Ð	200	4
1,2,3,6,7,8-HxCDD	Ð	Ð	200	4
1,2,3,7,8,9-HxCDD	Ð	Ð	200	4
1,2,3,4,7,8-HxCDF	Ð	Ð	200	4
1,2,3,6,7,8-HxCDF	Ð	Ð	200	4
1,2,3,7,8,9-HxCDF	Ð	Ð	200	4
2,3,4,6,7,8-HxCDF	Ð	Ð	200	4
1,2,3,4,6,7,8-HpCDD	Ð	Ð	200	4
1,2,3,4,6,7,8-HpCDF	Ð	Ð	200	4
1,2,3,4,7,8,9-HpCDF	Ð	Ð	200	4
OCDD	Ð	Ð	400	8
OCDF	Ð	Ð	400	8
$^{13}C_{12}$-2,3,7,8-TCDD	100	2	Ð	Ð
$^{13}C_{12}$-2,3,7,8-TCDF	100	2	Ð	Ð
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	2	Ð	Ð
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	2	Ð	Ð
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	2	Ð	Ð
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	2	Ð	Ð
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	2	Ð	Ð
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	2	Ð	Ð
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	2	Ð	Ð
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	2	Ð	Ð
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	2	Ð	Ð
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	2	Ð	Ð
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	2	Ð	Ð
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	2	Ð	Ð
$^{13}C_{12}$-OCDD	200	4	Ð	Ð

TABLE 3. CONCENTRATION OF STOCK AND SPIKING SOLUTIONS CONTAINING CDDS/CDFS AND LABELED COMPOUNDS

CDD/CDF	Labeled Compound Stock Solution [1] (ng/mL)	Labeled Compound Spiking Solution [2] (ng/mL)	PAR Stock Solution [3] (ng/mL)	PAR Spiking Solution [4] (ng/mL)
	Concentration (ng/mL)			
Cleanup Standard [5]				
$^{37}Cl_4$-2,3,7,8-TCDD	0.8			
Internal Standards [6]				
$^{13}C_{12}$-1,2,3,4-TCDD	200			
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	200			

[1] Section 7.10Ðprepared in nonane and diluted to prepare spiking solution.
[2] Section 7.10.3Ðprepared in acetone from stock solution daily.
[3] Section 7.9Ðprepared in nonane and diluted to prepare spiking solution.
[4] Section 7.14Ðprepared in acetone from stock solution daily.
[5] Section 7.11Ðprepared in nonane and added to extract prior to cleanup.
[6] Section 7.12Ðprepared in nonane and added to the concentrated extract immediately prior to injection into the GC (Section 14.2).

TABLE 4. CONCENTRATION OF CDDS/CDFS IN CALIBRATION AND CALIBRATION VERIFICATION SOLUTIONS[1] (section 15.3)

	CDD/CDF	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
2,3,7,8-TCDD	0.5	2	10	40	200
2,3,7,8-TCDF	0.5	2	10	40	200
1,2,3,7,8-PeCDD	2.5	10	50	200	1000
1,2,3,7,8-PeCDF	2.5	10	50	200	1000
2,3,4,7,8-PeCDF	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000
2,3,4,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000
OCDD	5.0	20	100	400	2000
OCDF	5.0	20	100	400	2000
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-PeCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
Cleanup Standard					
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2	10	40	200
Internal Standards					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 5. GC RETENTION TIME WINDOW DEFINING SOLUTION AND ISOMER SPECIFICITY TEST STANDARD (SECTION 7.15)

DB-5Column GC Retention-TimeWindow Defining Solution		
CDD/CDF	**First Eluted**	**Last Eluted**
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

DB-5Column TCDD Specificity Test Standard

1,2,3,7+1,2,3,8-TCDD
2,3,7,8-TCDD
1,2,3,9-TCDD

DB-225Column TCDF Isomer Specificity Test Standard

2,3,4,7-TCDF
2,3,7,8-TCDF
1,2,3,9-TCDF

TABLE 6. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ALL CDDS/CDFS ARE TESTED [1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3] s (ng/mL)	IPR [2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.8	8.3±12.9	6.7±15.8	7.8±12.9
2,3,7,8-TCDF	10	2.0	8.7±13.7	7.5±15.8	8.4±12.0
1,2,3,7,8-PeCDD	50	7.5	38±66	35±71	39±65
1,2,3,7,8-PeCDF	50	7.5	43±62	40±67	41±60
2,3,4,7,8-PeCDF	50	8.6	36±75	34±80	41±61
1,2,3,4,7,8-HxCDD	50	9.4	39±76	35±82	39±64
1,2,3,6,7,8-HxCDD	50	7.7	42±62	38±67	39±64
1,2,3,7,8,9-HxCDD	50	11.1	37±71	32±81	41±61
1,2,3,4,7,8-HxCDF	50	8.7	41±59	36±67	45±56
1,2,3,6,7,8-HxCDF	50	6.7	46±60	42±65	44±57
1,2,3,7,8,9-HxCDF	50	6.4	42±61	39±65	45±56
2,3,4,6,7,8-HxCDF	50	7.4	37±74	35±78	44±57
1,2,3,4,6,7,8-HpCDD	50	7.7	38±65	35±70	43±58
1,2,3,4,6,7,8-HpCDF	50	6.3	45±56	41±61	45±55
1,2,3,4,7,8,9-HpCDF	50	8.1	43±63	39±69	43±58
OCDD	100	19	89±127	78±144	79±126
OCDF	100	27	74±146	63±170	63±159
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28±134	20±175	82±121
$^{13}C_{12}$-2,3,7,8-TCDF	100	35	31±113	22±152	71±140
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	39	27±184	21±227	62±160
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	34	27±156	21±192	76±130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	38	16±279	13±328	77±130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	41	29±147	21±193	85±117
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	38	34±122	25±163	85±118
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	43	27±152	19±202	76±131
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	35	30±122	21±159	70±143
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	40	24±157	17±205	74±135
$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	100	37	29±136	22±176	73±137
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	35	34±129	26±166	72±138
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	41	32±110	21±158	78±129
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	40	28±141	20±186	77±129
$^{13}C_{12}$-OCDD	200	95	41±276	26±397	96±415
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.6	3.9±15.4	3.1±19.1	7.9±12.7

[1] All specifications are given as concentration in the final extract, assuming a 20 µL volume.
[2] s = standard deviation of the concentration.
[3] X = average concentration.

TABLE 6A. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ONLY TETRA COMPOUNDS ARE TESTED [1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3] s (ng/mL)	IPR [2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.7	8.7±12.4	7.3±14.6	8.2±12.3
2,3,7,8-TCDF	10	2.0	9.1±13.1	8.0±14.7	8.6±11.6
$^{13}C_{12}$-2,3,7,8-TCDD	100	35	32±115	25±141	85±117
$^{13}C_{12}$-2,3,7,8-TCDF	100	34	35±99	26±126	76±131
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.4	4.5±13.4	3.7±15.8	8.3±12.1

[1] All specifications are given as concentration in the final extract, assuming a 20 µL volume.
[2] s = standard deviation of the concentration.
[3] X = average concentration.

TABLE 7. LABELED COMPOUND RECOVERY IN SAMPLES WHEN ALL CDDS/CDFS ARE TESTED

Compound	Test Conc. (ng/mL)	Labeled Compound Recovery (ng/mL) [1]	Labeled Compound Recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	25±164	25±164
$^{13}C_{12}$-2,3,7,8-TCDF	100	24±169	24±169
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25±181	25±181
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24±185	24±185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21±178	21±178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32±141	32±141
$^{13}C_{12}$-1,2,3,6,7,8,-HxCDD	100	28±130	28±130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26±152	26±152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26±123	26±123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	29±147	29±147
$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	100	28±136	28±136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23±140	23±140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28±143	28±143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26±138	26±138
$^{13}C_{12}$-OCDD	200	34±313	17-157
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.5±19.7	35-197

[1] Specification given as concentration in the final extract, assuming a 20-µL volume.

TABLE 7A. LABELED COMPOUND RECOVERY IN SAMPLES WHEN ONLY TETRA COMPOUNDS ARE TESTED

Compound	Test Conc. (ng/mL)	Labeled compound recovery	
		(ng/mL) [1]	(%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	31-137	31-137
$^{13}C_{12}$-2,3,7,8-TCDF	100	29-140	29-140
$^{37}Cl_4$-2,3,7,8-TCDD	10	4.2±16.4	42±164

[1] Specification given as concentration in the final extract, assuming a 20 µL volume.

TABLE 8. DESCRIPTORS, EXACT M/Z's, M/Z TYPES, AND ELEMENTAL COMPOSITIONS OF THE CDDs AND CDFs

Descriptor	Exact M/Z [1]	M/Z Type	Elemental Composition	Substance [2]
1	292.9825	Lock	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF[3]
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF[3]
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD[4]
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD[3]
	333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD[3]
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
2	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF [3]
	354.9792	Lock	C_9F_{13}	PFK
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD [3]
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD [3]
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF [3]
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF [3]
	389.8157	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD

TABLE 8. DESCRIPTORS, EXACT M/Z's, M/Z TYPES, AND ELEMENTAL COMPOSITIONS OF THE CDDs AND CDFs

Descriptor	Exact M/Z [1]	M/Z Type	Elemental Composition	Substance [2]
	392.9760	Lock	C_9F_{15}	PFK
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD [3]
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD [3]
	430.9729	QC	C_9F_{17}	PFK
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
4	407.7818	M+2	$C_{12}H{}^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H{}^{35}Cl_7O$	HpCDF [3]
	419.8220	M+2	$^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO$	HpCDF [3]
	423.7766	M+2	$C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	430.9729	Lock	C_9F_{17}	PFK
	435.8169	M+2	$^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD [3]
	437.8140	M+4	$^{13}C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD [3]
	479.7165	M+4	$C_{12}H{}^{35}Cl_7{}^{37}Cl_2O$	NCDPE
5	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	442.9728	Lock	$C_{10}F_{17}$	PFK
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD [3]
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD [3]
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE

[1] Nuclidic masses used:

H = 1.007825 C = 12.00000 ^{13}C = 13.003355 F = 18.9984
O = 15.994915 ^{35}Cl = 34.968853 ^{37}Cl = 36.965903

[2]
TCDD = Tetrachlorodibenzo-*p*-dioxin TCDF = Tetrachlorodibenzofuran
PeCDD = Pentachlorodibenzo-*p*-dioxin PeCDF = Pentachlorodibenzofuran
HxCDD = Hexachlorodibenzo-*p*-dioxin HxCDF = Hexachlorodibenzofuran
HpCDD = Heptachlorodibenzo-*p*-dioxin HpCDF = Heptachlorodibenzofuran
OCDD = Octachlorodibenzo-*p*-dioxin OCDF = Octachlorodibenzofuran
HxCDPE = Hexachlorodiphenyl ether HpCDPE = Heptachlorodiphenyl ether
OCDPE = Octachlorodiphenyl ether NCDPE = Nonachlorodiphenyl ether
DCDPE = Decachlorodiphenyl ether PFK = Perfluorokerosene

[3] Labeled compound.

[4] There is only one m/z for $^{37}Cl_4$-2,3,7,8,-TCDD (cleanup standard).

TABLE 9. THEORETICAL ION ABUNDANCE RATIOS AND QC LIMITS

Number of Chlorine Atoms	M/Z Ions Forming Ratio	Theoretical Ratio	QC Limit [1]	
			Lower	Upper
4 [2]	M/(M+2)	0.77	0.65	0.89
5	(M+2)/(M+4)	1.55	1.32	1.78
6	(M+2)/(M+4)	1.24	1.05	1.43
6 [3]	M/(M+2)	0.51	0.43	0.59
7	(M+2)/(M+4)	1.05	0.88	1.20
7 [4]	M/(M+2)	0.44	0.37	0.51
8	(M+2)/(M+4)	0.89	0.76	1.02

[1] QC limits represent ±15% windows around the theoretical ion abundance ratios.
[2] Does not apply to $^{37}Cl_4$-2,3,7,8-TCDD (cleanup standard).
[3] Used for $^{13}C_{12}$-HxCDF only.
[4] Used for $^{13}C_{12}$-HpCDF only.

TABLE 10. SUGGESTED SAMPLE QUANTITIES TO BE EXTRACTED FOR VARIOUS MATRICES [1]

Sample Matrix [2]	Example	Percent Solids	Phase	Quantity Extracted
Single-phase				
Aqueous	Drinking water Groundwater Treated wastewater	<1	Đ [3]	1000 mL
Solid	Dry soil Compost Ash	>20	Solid	10 g
Organic	Waste solvent Waste oil Organic polymer	<1	Organic	10 g
Tissue	Fish Human adipose	Đ	Organic	10 g
Multi-phase				
Liquid/Solid				
Aqueous/Solid	Wet soil Untreated effluent Digested municipal sludge Filter cake Paper pulp	1±30	Solid	10 g
Organic/solid	Industrial sludge Oily waste	1±100	Both	10 g
Liquid/Liquid				
Aqueous/organic	In-processeffluent Untreated effluent Drum waste	<1	Organic	10 g
Aqueous/organic/solid	Untreated effluent Drum waste	>1	Organic & solid	10 g

[1] The quantitity of sample to be extracted is adjusted to provide 10 g of solids (dry weight). One liter of aqueous samples containing 1% solids will contain 10 g of solids. For aqueous samples containing greater than 1% solids, a lesser volume is used so that 10 g of solids (dry weight) will be extracted.

[2] The sample matrix may be amorphous for some samples. In general, when the CDDs/CDFs are in contact with a multiphase system in which one of the phases is water, they will be preferentially dispersed in or adsorbed on the alternate phase because of their low solubility in water.

[3] Aqueous samples are filtered after spiking with the labeled compounds. The filtrate and the materials trapped on the filter are extracted separately, and the extracts are combined for cleanup and analysis.

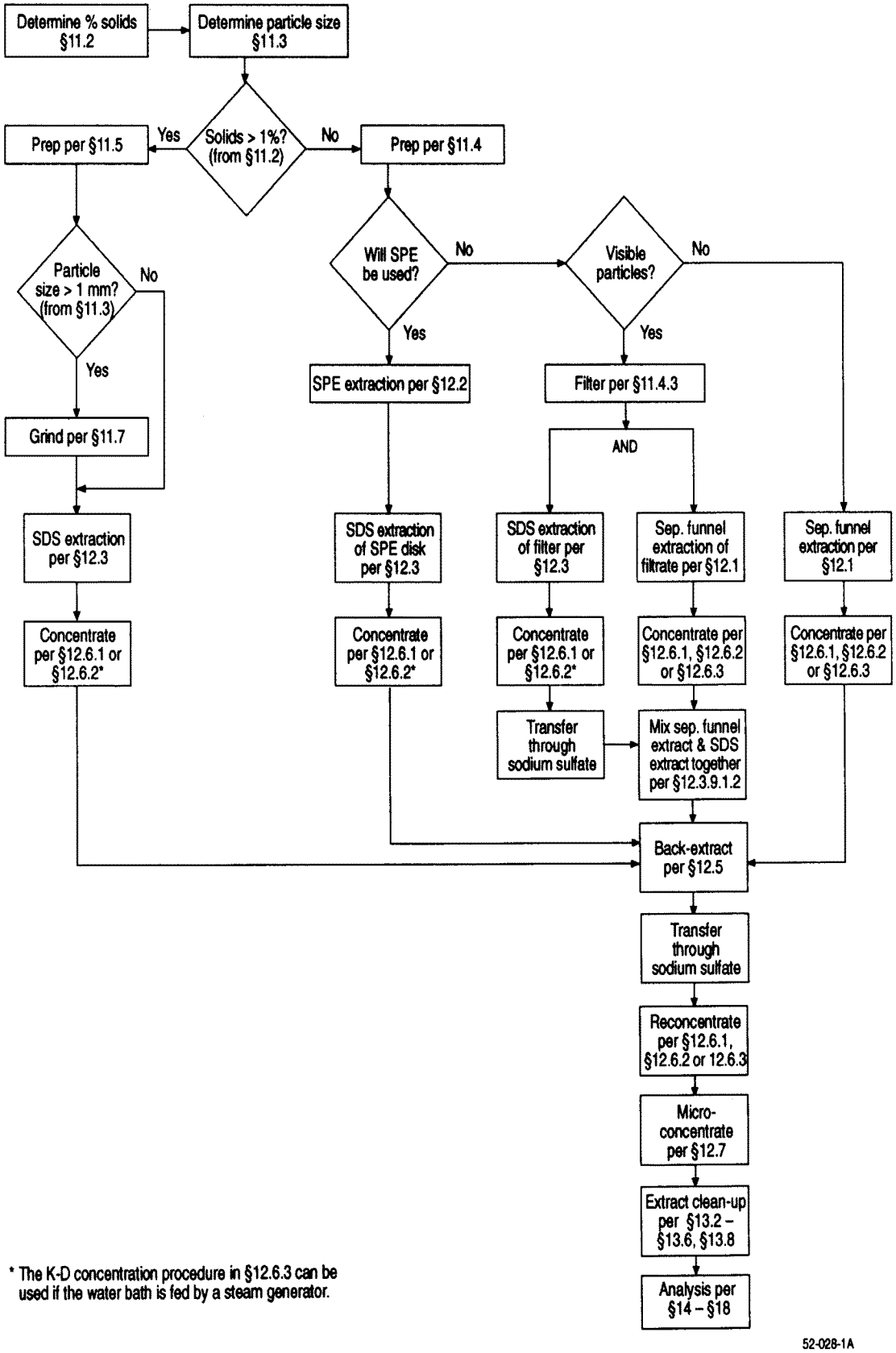


Figure 1. Flow Chart for Analysis of Aqueous and Solid Samples

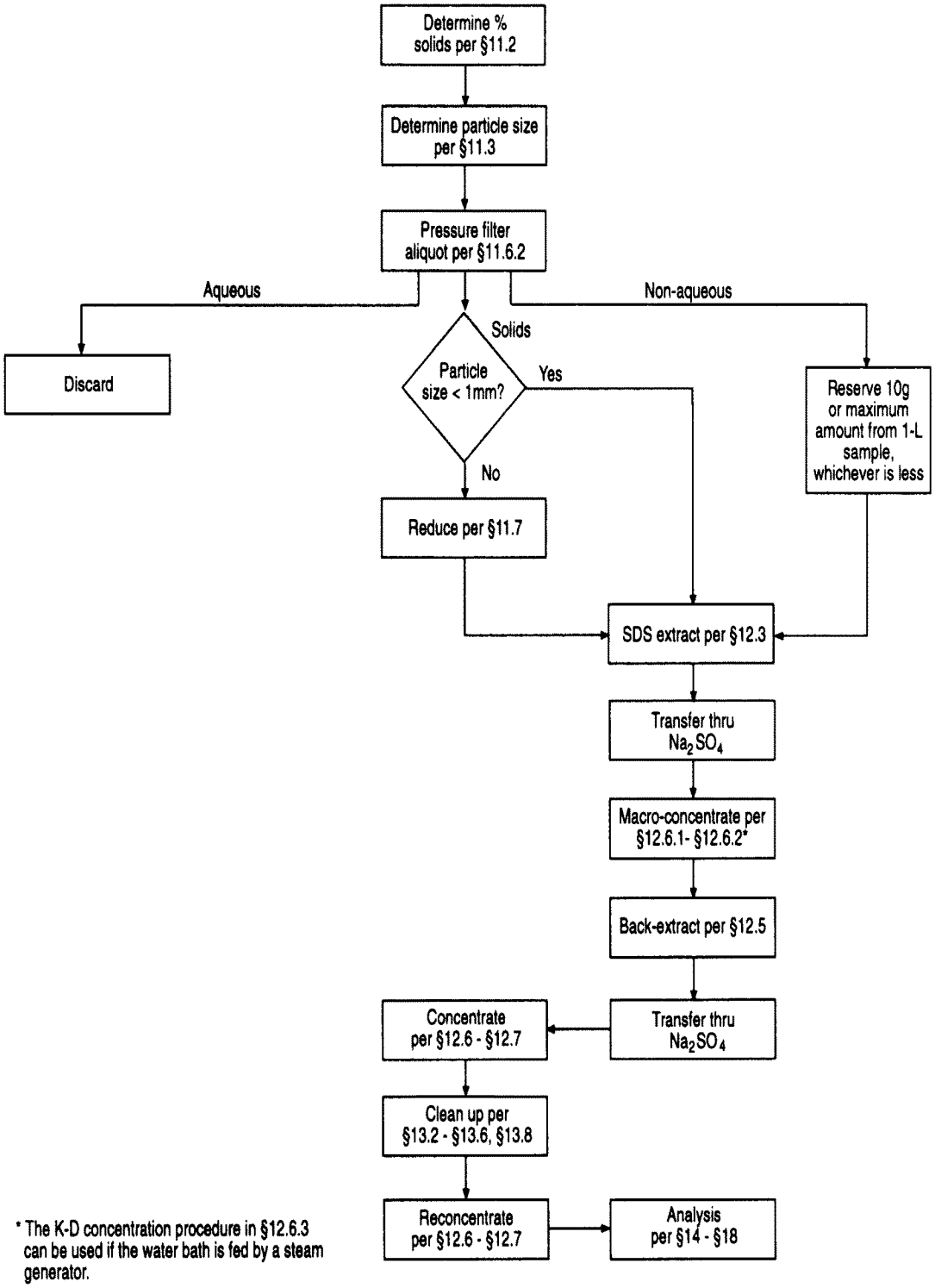


Figure 2. Flow Chart for Analysis of Multi-Phase Samples

52-028-2A

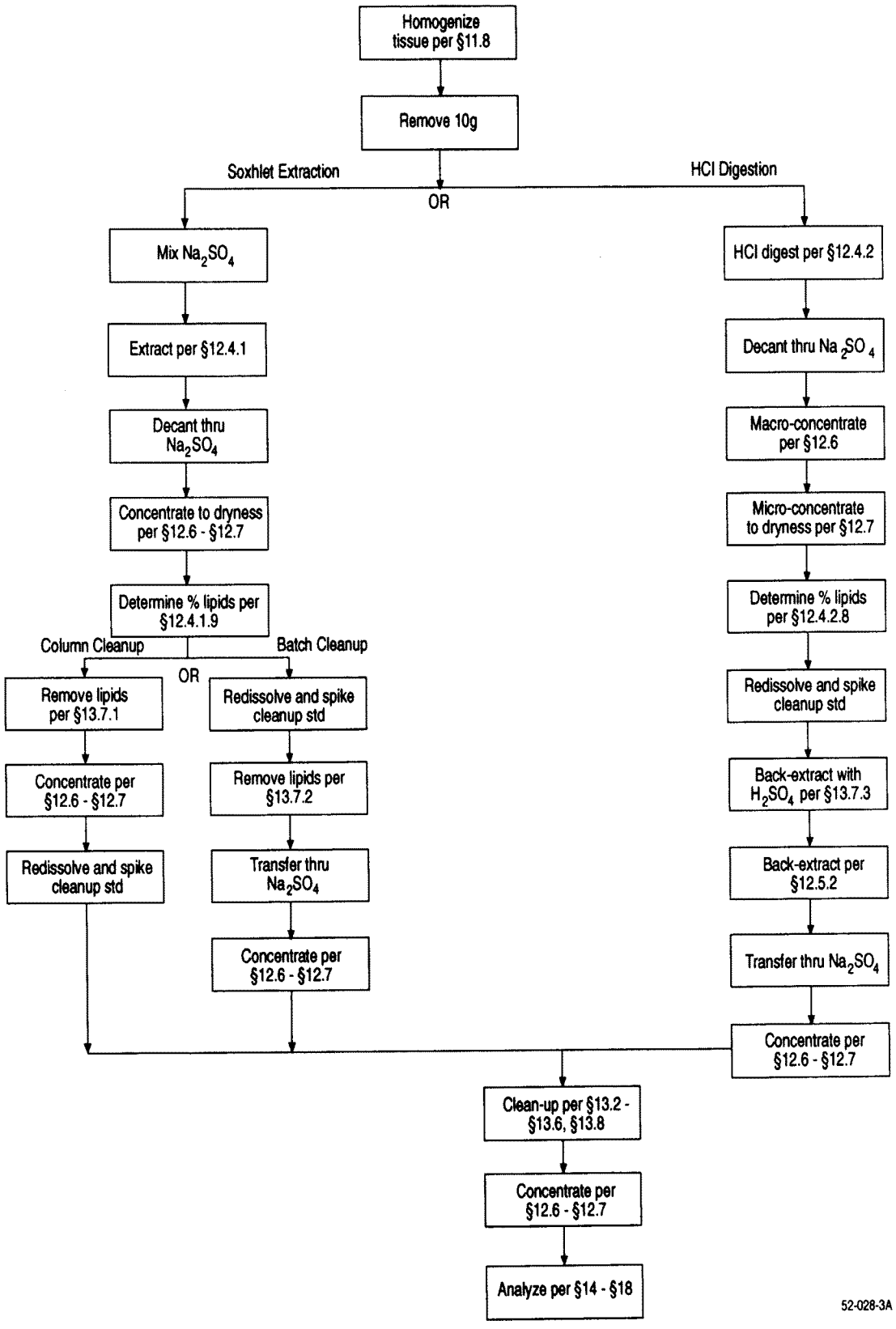


Figure 3. Flow Chart for Analysis of Tissue Samples

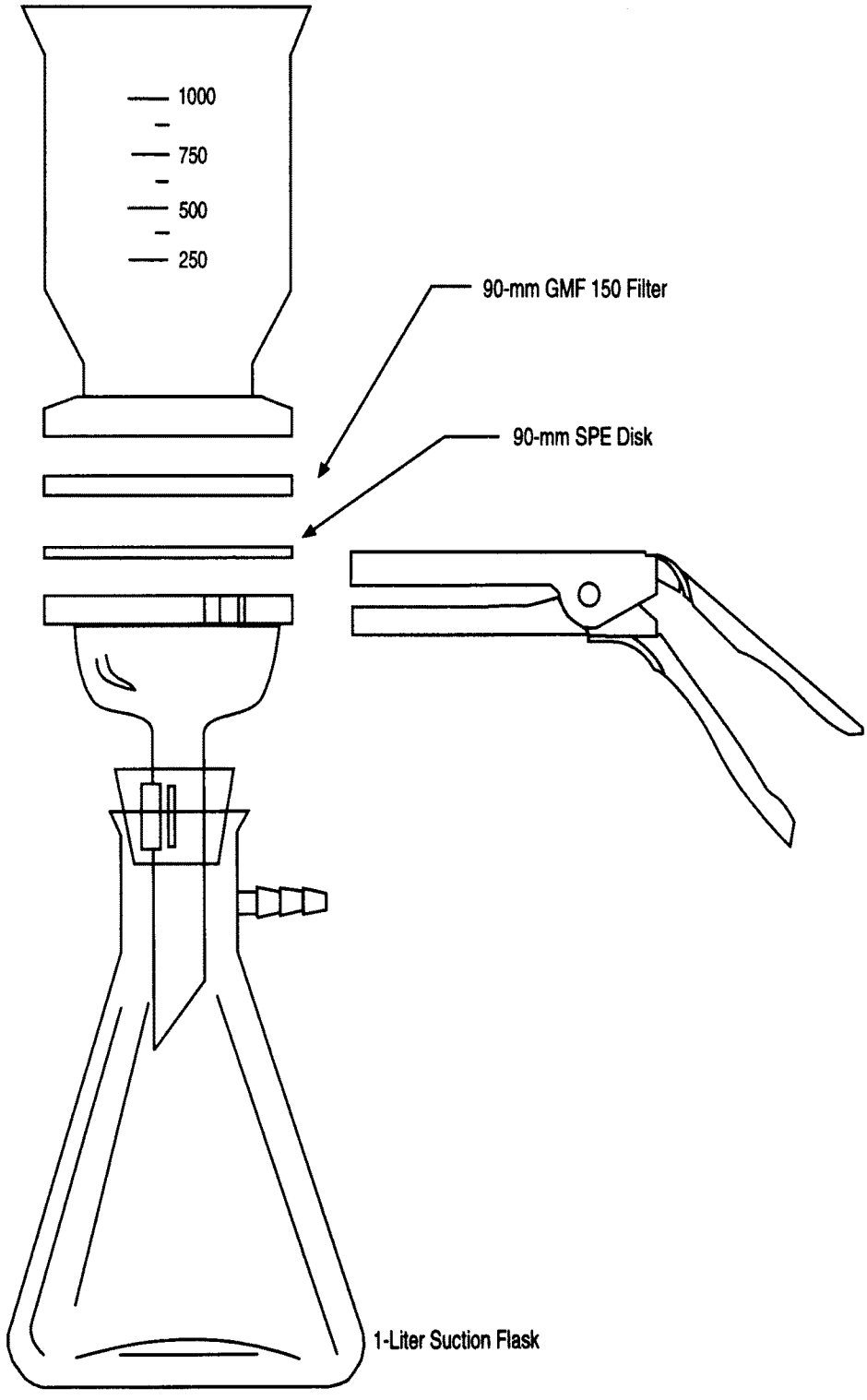
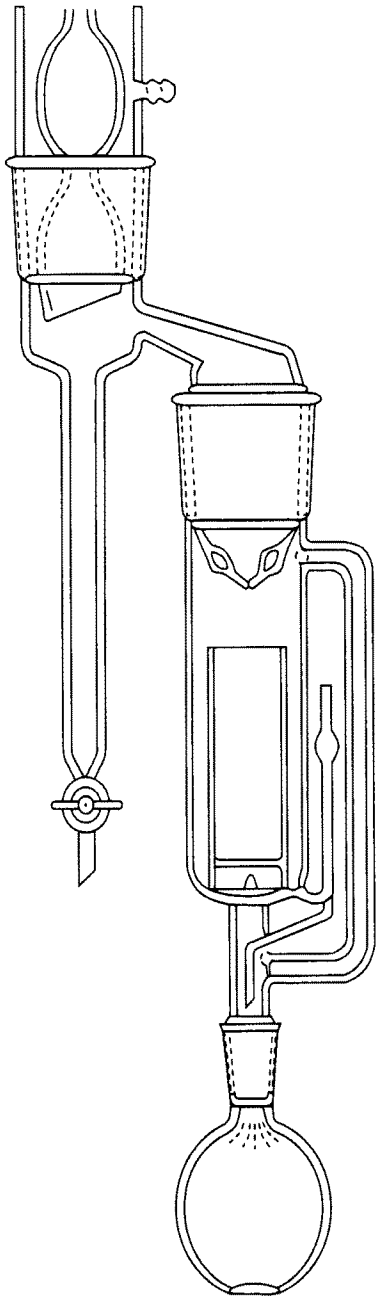


Figure 4. Solid-Phase Extraction Apparatus

52-027-1A



52-027-2A

Figure 5. Soxhlet/Dean-Stark Extractor

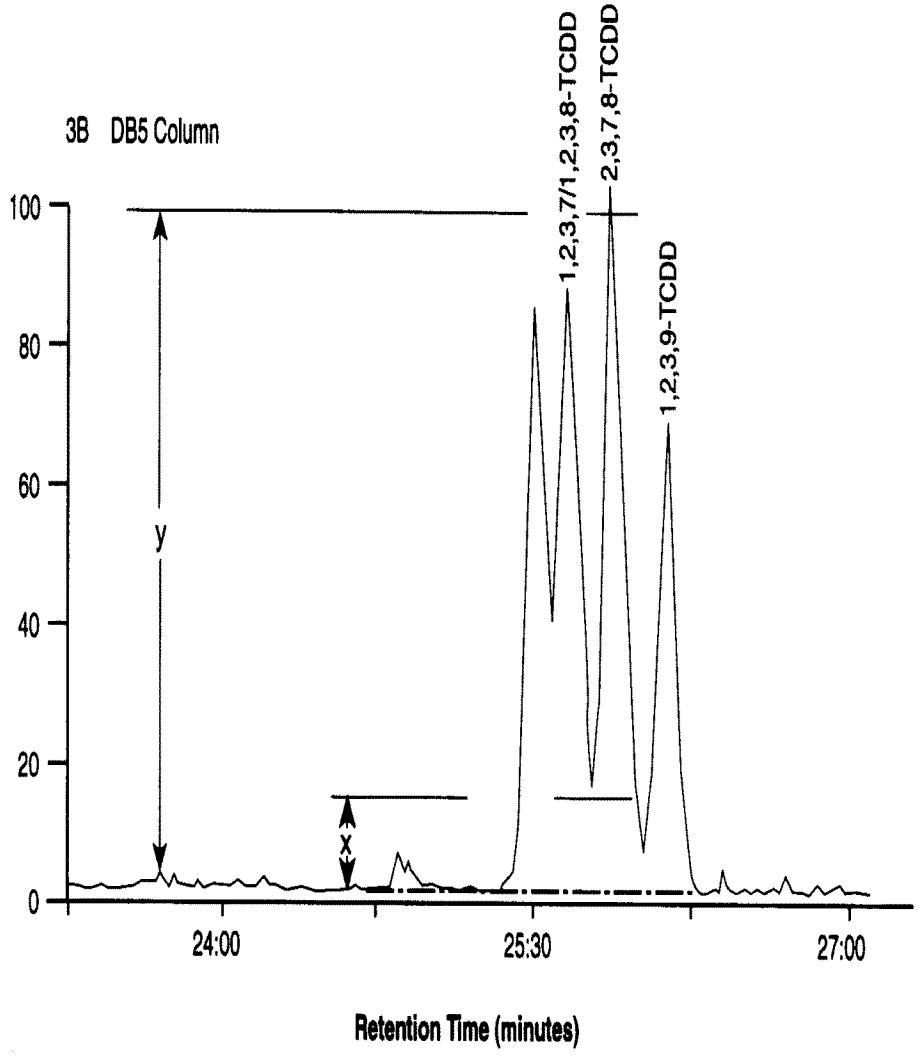


Figure 6. Isomer-Specific Separation of 2,3,7,8-TCDD on DB-5 Column

52-027-03

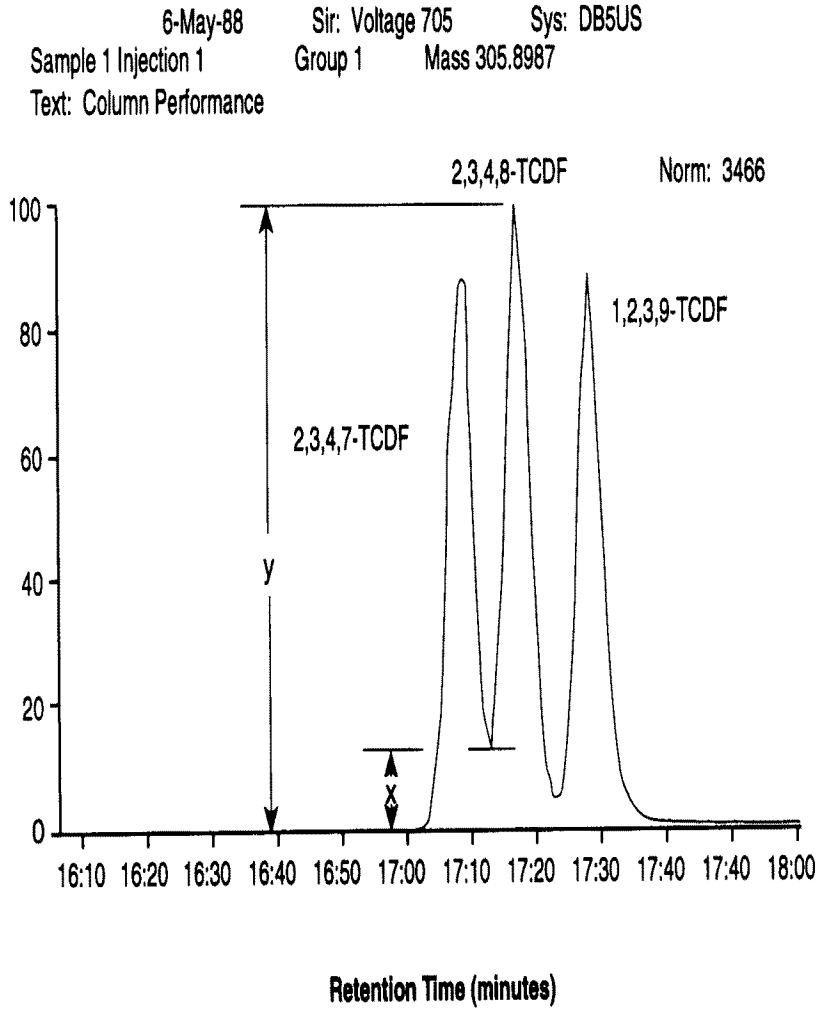


Figure 7. Isomer-Specific Separation of 2,3,7,8-TCDF on DB-5 Column

52-027-4A

24.0 Glossary of Definitions and Purposes

These definitions and purposes are specific to this method but have been conformed to common usage as much as possible.

24.1 Units of weight and Measure and Their Abbreviations

24.1.1 Symbols

°C	degrees Celsius
µL	microliter
µm	micrometer
<	less than
>	greater than
%	percent

24.1.2 Alphabetical abbreviations

amp	ampere
cm	centimeter
g	gram
h	hour
ID	inside diameter
in.	inch
L	liter
M	Molecular ion
m	meter
mg	milligram
min	minute
mL	milliliter
mm	millimeter
m/z	mass-to-charge ratio
N	normal; gram molecular weight of solute divided by hydrogen equivalent of solute, per liter of solution
OD	outside diameter
pg	picogram
ppb	part-per-billion
ppm	part-per-million
ppq	part-per-quadrillion
ppt	part-per-trillion
psig	pounds-per-square inch gauge
v/v	volume per unit volume
w/v	weight per unit volume

24.2 Definitions and Acronyms (in Alphabetical Order)

AnalyteÐA CDD or CDF tested for by this method. The analytes are listed in Table 1.

Calibration Standard (CAL)ÐA solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration.

Calibration Verification Standard (VER)ÐThe mid-pointcalibration standard (CS3) that is used in to verify calibration. See Table 4.

CDDÐChlorinated Dibenzo-*p*-ioxinÐThe isomers and congeners of tetra-through octa-chlorodibenzo-*p*-dioxin.

CDFÐChlorinated DibenzofuranÐThe isomers and congeners of tetra-through octa-chlorodibenzofuran.

CS1, CS2, CS3, CS4, CS5ÐSee Calibration standards and Table 4.

Field BlankÐAn aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

GCÐGas chromatograph or gas chromatography.

GPCÐGel permeation chromatograph or gel permeation chromatography.

HPLCÐHigh performance liquid chromatograph or high performance liquid chromatography.

HRGCÐHigh resolution GC.

HRMSÐHigh resolution MS.

IPRÐInitial precision and recovery; four aliquots of the diluted PAR standard analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.

K-DÐKuderna-Danish concentrator; a device used to concentrate the analytes in a solvent.

Laboratory BlankÐSee method blank.

Laboratory Control sample (LCS)ÐSee ongoing precision and recovery standard (OPR).

Laboratory Reagent BlankÐSee method blank.

MayÐThis action, activity, or procedural step is neither required nor prohibited.

May NotÐThis action, activity, or procedural step is prohibited.

Method BlankÐAn aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

Minimum Level (ML)ÐThe level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

MSÐMass spectrometer or mass spectrometry.

MustÐThis action, activity, or procedural step is required.

OPRÐOngoing precision and recovery standard (OPR); a laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

PARÐPrecision and recovery standard; secondary standard that is diluted and spiked to form the IPR and OPR.

PFKÐPerfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

Preparation BlankÐSee method blank.

Primary Dilution StandardÐA solution containing the specified analytes that is purchased or prepared from stock solutions and diluted as needed to prepare calibration solutions and other solutions.

Quality Control Check Sample (QCS)ÐA sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

Reagent WaterÐWater demonstrated to be free from the analytes of interest and potentially interfering substances at the method detection limit for the analyte.

Relative Standard Deviation (RSD)ÐThe standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

RFÐResponse factor. See Section 10.6.1.

RRÐRelative response. See Section 10.5.2.

RSDÐSee relative standard deviation.

SDSÐSoxhlet/Dean-Stark extractor; an extraction device applied to the extraction of solid and semi-solid materials (Reference 7).

ShouldÐThis action, activity, or procedural step is suggested but not required.

SICPÐSelected ion current profile; the line described by the signal at an exact m/z.

SPEÐSolid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

Stock SolutionÐA solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

TCDDÐTetrachlorodibenzo-*p*-dioxin.

TCDFÐTetrachlorodibenzofuran.

VERÐSee calibration verification standard.

Analytical Method SOP
No. L-3

ALS SOP 739 Rev. 10 and 713
Rev. 12

ALS
STANDARD OPERATING PROCEDURE 739 REVISION 10

TITLE: PREPARATION OF SAMPLES FOR ANALYSIS BY GAMMA SPECTROSCOPY

FORMS:

APPROVED BY:

TECHNICAL MANAGER _____ DATE _____
QUALITY ASSURANCE MANAGER _____ DATE _____
LABORATORY MANAGER _____ DATE _____

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps used to prepare soil, water and sludge samples for gamma spectroscopy analysis. Vegetation, air filter and bioassay samples are not addressed in this SOP, and must be handled on a case-by-case basis.

2. SUMMARY

Soils and sludges are prepared (i.e., dried and sieved) per SOP 736, prior to beginning the procedure outlined in this SOP. Some soils and sludges may omit such preparations if approval is given by the or Project Manager. Waters are either filtered or left unfiltered prior to preparation as per work order or Radiochemistry Manager instructions. Waters are measured volumetrically into an appropriately sized Marinelli beaker. Soils are measured gravimetrically into a Lermer jar or a steel can, as appropriate for the sample size and the analyte. The gamma spec containers are sealed with their lids, and wiped with a damp paper towel to remove potential contamination.

3. RESPONSIBILITIES

3.1 It is the responsibility of the technician to perform these procedures according to this SOP and to complete all documentation required for review.

3.2 These procedures are to be performed only by personnel who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.3 It is the responsibility of the analyst to be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOP 715 as well as the LIMS program specification related to the client, project, and test method being performed.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events. Any discrepancies must

be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 Gamma spec samples must be produced only in the specific geometry for which the Instrumentation Group has calibrated their spectrometers.

4.2 New containers ordered for gamma spec must be equivalent to those currently in use. The Radiochemistry Manager or designee must approve the use of alternate containers or supplies in advance.

4.3 Gamma spec containers are not reusable due to the possibility of carry-over in the next analysis. Once the analysis is complete, the container is returned to the sample storage area.

4.4 The prep and instrumentation technicians maintain the internal Chain of Custody (COC). When the original client sample container is taken by a prep technician from the sample storage area, he/she logs the sample out as normal. Because gamma spec is a non-destructive test, samples that are designated for other (non-volatile) tests may be used. Check with Group Leaders if there are questions concerning sample availability or if samples are turn-around-time sensitive.

4.5 The prep technician is responsible for creating a gamma fraction for chain of custody. The prep analyst logs out the gamma container on behalf of the counting room analyst and relinquishes the sample along with the benchsheet. After counting, the gamma spec analyst will return the samples to the sample storage area and check them in. If the aliquot taken for gamma spec is needed for other analyses, log in/log out activities are managed by barcode scanning (COC SOP 318).

4.6 The standard filter geometry is a 47mm diameter filter mounted in a 2" stainless steel planchet. For Ra-226 analysis of a solid/soil sample, the packing must be done in a can as a geometry (GEO) 17. Usually the can packing will be done on an "As Received" basis, and the % moisture data will be provided to report on a dry weight basis. If the sample volume is limited, regular Gamma can be packed as a GEO 11 and the "Ra-can" could be packed with the available sample. If the can is not filled to the top, the technician should mark a line on the outside of the container indicating the height of the actual sample and write a Quality Assurance Summary Sheet (QASS), Form 302. This documentation will be included in the final report.

4.7 Filter samples can be digested using SOP 773 or SOP 767, then the digestate is diluted to 1000mL with DI water and packed for Gamma as GEO 1. Samples like vegetation, debris, gloves, wipes, iron bar, lead blocks, ashes, fruits, fish, cloth, wood chips etc., will be treated with different methods based on the nature of the samples and conditions. The samples may be leached using different acids or

digested and packed with different GEO. However, all geometry preparations will be documented on a QASS and a copy will be attached to the benchsheet.

5. APPARATUS AND MATERIALS

5.1 Balance, top loading, 0.01g sensitivity

5.2 Scoops, spatulas, tongue depressors

5.3 Graduated cylinders, type TD (to deliver), 1L

5.4 Marinelli beakers with lids, Ga-ma # 138G, or equivalent *, 2L

5.5 Lermer Jars with 89mm screw lid, plastic, or equivalent *, 16oz

5.6 Large funnel, glass/plastic

5.7 Vinyl tape

5.8 Parafilm™

5.9 Qualitative filter paper, fluted, VWR brand #313 or equivalent

5.10 Cans for Geo 17, House of Cans #3104 or equivalent *

* ***Equivalent containers require approval by the Radiochemistry Manager or designee.***

6. REAGENTS

Deionized (DI) water, obtained from the laboratory's DI water system

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Samples may be collected in any type of glass or plastic container.

7.2 Aqueous samples should be preserved to pH<2 with nitric acid.

7.3 If samples are to be stored for an extended period of time, refrigeration is recommended to prevent biological growth in the sample.

7.4 At the current time, there is no regulatory holding time established for gamma analysis. Many sampling and analysis plans, however, apply a default holding time of 180 days from date of collection. If samples are analyzed more than 180 days after collection, this fact should be noted in the laboratory data package case narrative.

8. PROCEDURE

8.1 PROCEDURE FOR WATER SAMPLES

8.1.1 Samples must be properly preserved before aliquotting. Verify that the pH is less than 2, per SOP 733. If the sample contains visible sediment or other conditions exist that make preservation impractical, notify the Project Manager (PM) of the lab's intent to proceed with analysis of

the unpreserved sample and document the situation on a Quality Assurance Summary Sheet (Form 302).

8.1.2 Do not prepare water samples in the same workspace where soil samples are being prepared. This avoids cross-contamination by dust.

8.1.3 If the sample contains sediment or suspended solids, check the work order for specific instructions as to whether or not the sample should be filtered. If it is not specified, filter per SOP 736. If the project instructions specify "Dissolved" or "Filtered", filter the sample through a fluted filter into a clean 1L graduated cylinder. Pre-filtering may be required for especially turbid samples. If the project instructions specify "Total" or "As Received," shake the sample container to mix thoroughly and aliquot as received.

8.1.4 Liquid samples are prepared in 2L Marinelli beakers. Measure the appropriate volume of water sample in a clean 1L type TD graduated cylinder to the nearest 0.01L (i.e., 10mL). Empty the sample into a clean, labeled Marinelli beaker.

8.1.5 The gravimetric method is adapted for liquid samples other than water. Place an empty Marinelli beaker on the top loading balance and tare the balance to zero. Add the sample slowly into the Marinelli beaker until the final weight is 1000 + 0.01g.

NOTE: If the sample volume provided falls short of the desired geometry, dilute to the appropriate geometry with DI water (e.g., dilute 600mL to 1L). *Make sure to record the original volume on the container and on the benchsheet.*

8.1.6 A method blank is made by adding a representative volume of DI water to an empty, labeled Marinelli beaker. Refer to SOP 715 to determine the aliquot size for the blank. The collection date for the blank is the date the samples are packed.

8.1.7 A Laboratory Control Sample (LCS) needs to be created on the benchsheet for every batch of twenty samples. The prep technician does not physically prepare the LCS, instead, the gamma spec analyst uses a pre-made, independent second source LCS obtained from an outside vendor. The information to be filled in on the benchsheet for the LCS varies depending on the GEO size. For waters, indicate the following:

GEO NUMBER	LCS ALIQ.SIZE
1	1000 mL

8.1.8 Attach the lid of the Marinelli beaker and seal the lid using vinyl tape. Wipe the exterior of the container with a damp paper towel to remove potential contamination. Make sure the container is labeled with the sample ID, aliquot size, date of prep and initials.

8.1.9 Submit the prepared samples to the counting room. The counting room will analyze the samples in the manner described in SOP 713. Upon completion of gamma counting, the sample fraction will be returned to the sample storage area and the gamma spec analyst will check the sample back in to the storage area per COC SOP 318 procedures.

8.2 PROCEDURE FOR SOIL AND SLUDGE SAMPLES

8.2.1 Unless approval to the contrary is given, all soil samples must be dried and sieved through a number 4 sieve prior to preparation for gamma spec analysis. Consult SOP 736 for drying and sieving procedures.

Containers for gamma spec soils are usually prepared when the soil is being prepared for other analyses under SOP 736. The gamma spec prep worksheet for soils should be filled out manually by the prep technician at the time of packing gamma, and the electronic benchsheet will be created later on. The prep worksheet will be attached to the benchsheet when the sample is relinquished to the counting room.

The benchsheet provides information about the prep date, technician, balance number, report basis, etc., as well as all the information about how the sample was packed. Any unusual situation will be documented on a QASS (Form 302).

8.2.2 When using Lermer jars, fill the container to the appropriate level according to the desired geometry. If enough sample is provided, use Geometry 13 (500g). If not, reduce the sample volume to Geometry 11 (100g).

8.2.2.1 Sample volumes should be maintained to within ½ cm of the correct geometry height in the container.

8.2.2.2 Zero out the container weight on the balance prior to weighing out a sample..

8.2.2.3 Soil samples should be well settled into their containers by gentle shaking with the lid on. Do not pack or compress soils into the containers.

8.2.2.4 Consult the Radiochemistry Manager or Group Leader if the sample volume provided is less than a Geometry 11. The analysis will usually still be conducted, but the Project

Manager will need to be informed because of the effects on the efficiency calibration and detection limits.

8.2.3 For Ra-226 analysis by gamma spec, the samples will be packed as a GEO 17. Generally, the samples will be packed on a "Dry" basis, however, due to rush turn around times, the sample can be packed "As Received". To accomplish this, transfer the sample to a steel can (appropriate for GEO 17), until it is filled to the top. Tap the can to remove air pockets and to settle the sample. Do not press or "pack" the sample into the can. Add more sample to fill the can to the top. To ensure a tight seal, place a piece of Parafilm over the top of the can then cap the can with the metal lid and seal with the can sealer. Remove any excess Parafilm™ from the outside of the can.

8.2.4 A Laboratory Control Sample (LCS) needs to be created on the benchsheet for every batch of twenty samples. The prep technician does not physically prepare the LCS, instead, the gamma spec analyst uses a pre-made LCS obtained from an outside vendor. The information to be filled in on the benchsheet for the LCS varies depending on the GEO size as follows:

GEO NUMBER	LCS ALIQ.SIZE
11	100g
13	500g
17	215g
26	215g
7	1s
8	1s
9	1s

8.2.5 After the preparation worksheet and the benchsheet are completed, fill out the LIMS tracking sheet, review the packet, and complete the tracking sheet.

8.2.6 Submit the samples prepared as above to the counting room. The counting room will analyze the samples in the manner described in SOP 713. Upon completion of gamma counting, the sample fraction will be returned to the sample storage area and the instrument analyst will check the sample back in to the storage area and fill out the internal COC.

8.3 CALCULATIONS

TPU FACTORS. As defined in SOP 708, the following preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty (TPU):

8.3.1 Water samples require a preparation uncertainty factor of 0.0504 at the one-sigma level. This is based on one gross aliquoting (sample homogeneity) and one volumetric measurement. See the following equation:

$$0.0504 = \sqrt{0.05^2 + 0.006^2}$$

8.3.2 Solid samples require a preparation uncertainty factor of 0.0501 at the one-sigma level. This is based on one gross aliquoting (sample homogeneity) and one mass measurement. See the following equation:

$$0.0501 = \sqrt{0.05^2 + 0.003^2}$$

8.3.3 In practice, these two TPU factors are substantially equivalent. To simplify the data reporting procedure, the greater of the two (0.0504) may be used for both matrices.

9. QUALITY CONTROL

Acceptance criteria for QC samples may vary per client specifications (typically controlled via test code nicknames), consult applicable LIMS program specification.

9.1 Method blanks will be run at a frequency of five-percent (i.e., one per 20 field samples) with a minimum of one per batch. Method blanks for water consist of deionized (DI) water. Method blanks for solid samples consist of an empty container, appropriate for the geometry (i.e., 13, 11, 17).

9.2 Laboratory Control Samples (LCS) will be run at a frequency of five-percent with a minimum of one per batch. The LCS consists of a pre-made source from an outside vendor.

9.3 Duplicate samples will be run at a frequency of ten-percent with a minimum of one per batch. If insufficient volume is available for a duplicate, a count duplicate may be used.

10. METHOD DEVIATIONS

SOP 739 is an ALS procedure and there are therefore no deviations from a reference method.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

All Safety and Hazards are managed in accordance with the current facility plans:

- Chemical Hygiene Plan (CHP)
- Radiation Protection Plan (RPP).
- Emergency and Contingency Plan (ECP)
- Respiratory Protection Plan (RESPP)

11.1 SAFETY AND HAZARDS

11.1.1 Soil samples should be handled in a hood as much as possible to avoid inhalation and cross contamination with dust. Workspaces should be wiped down with damp paper towels whenever dust is evident and always at the end of the shift.

11.1.2 ,

11.2 WASTE DISPOSAL
All wastes are disposed of according to the Waste Management Plan (WMP

12. REFERENCES

SOP 708, "Calculations for Radioanalytical Results."

ALS STANDARD OPERATING PROCEDURE 713 REVISION 12

TITLE: ANALYSIS OF GAMMA EMITTING RADIONUCLIDES BY GAMMA SPECTROSCOPY -- METHOD EPA 901.1

FORMS: APPENDIX E

APPROVED BY:

TECHNICAL MANAGER _____ DATE _____

QUALITY ASSURANCE MANAGER _____ DATE : _____

LABORATORY MANAGER _____ DATE _____

1 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary to perform gamma emissions analysis of samples of various media using high purity germanium (HPGe) high-resolution intrinsic gamma spectrometry. This procedure is applicable to all gamma spectrometry analyses performed at ALS. The procedures outlined in this SOP are based on EPA Method 901.1 and DOE/EML Procedure 4.5.2.3.

2 SUMMARY

Gamma emissions from radionuclides are detected by a semiconductor germanium crystal, which provides a small electronic pulse for each gamma interaction where the pulse height is proportional to the gamma incident energy. This electronic data is converted to digital data by an analog to digital converter (ADC) and stored in a multichannel buffer (MCB). The data collected by the MCB is subsequently interpreted by a complex software program, generating results in units of radioactivity per unit sample volume. The gamma spectroscopy analysis software program used is Seeker®, Version 2.2, a product of Vertechs Software Solution, Inc.

3 RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform these procedures according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of a proficiency test sample.

3.2 Upon receipt of a new or repaired detector, it is the responsibility of the technician to follow the steps outlined in Appendix D, 'General Gamma Detector Operations', prior to data acquisition.

3.3 It is the responsibility of all personnel who work with samples or data involving this method to consult the applicable LIMS Program Specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off of the data are performed by the Department Manager or designee. Initialing and dating the processed data indicates that this review for precision, accuracy, completeness and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving these procedures to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4 INTERFERENCES

The physical shape of the source and its proximity to the detector is critical to the efficiency calibration. These factors define the "counting geometry". The calibration geometry and the sample geometry must match within ±0.5cm of the line on the sample container.

5 APPARATUS AND MATERIALS

This procedure is conducted with the use of installed gamma detection and analysis equipment consisting of multiple intrinsic germanium gamma spectrometers mounted in lead shields for the reduction of ambient background radiation, a personal computer analysis system with multichannel analyzer interfaces, three NIM-bin based multichannel buffers, gamma analysis software, and associated nuclear electronics and cabling.

6 REAGENTS

No reagents are used by this procedure. The operator should be aware, however, that water samples are preserved to pH <2 with Nitric Acid (HNO_3).

7 PROCEDURE

7.1 OPERATING CONDITIONS

The gamma spectrometry systems shall be operated with detector bias as specified by the detector manufacturer and amplifier and MCB settings as required to obtain a nominal 0.5keV/channel energy calibration across a range of approximately 40 to 2000keV. The operating conditions shall be verified daily by performance of the daily quality control checks (described in Section 8 below).

7.2 SPECTRUM ACQUISITION

7.2.1 The detector must be calibrated for the geometry of the sample to be analyzed. Efficiency calibration procedures are defined in Section 8 below. A list of current geometries, calibration date and the dates the calibrations expire, as well as standards used for calibration is posted in the instrument lab. This list is maintained by instrument lab personnel and is exempt from 'Operator Aid' policies, as it is an integral part of gamma operations and is updated on an on-going basis.

Samples shall be placed directly on the detector, inside the lead shield, and in a manner that is level and centered over the detector, unless noted otherwise on a Quality Assurance Summary Sheet (QASS) or other supporting documentation.

7.2.2 After samples have been loaded on the detectors, select the desired detector in the Spectral Display Control menu. Next, select the 'TOOLS' icon, which will then prompt for the ID and the desired live time or count time.

Enter the sample ID as it appears on the sample benchsheet, followed by a space, and then the batch ID (e.g., 0011222-3 GSyymmdd-n). After the ID has been entered, select the 'ID SET' icon to save the sample ID.

Enter the desired count time in seconds in the box labeled 'LIVE TIME' and then select the 'PRE SET' icon to save the count time. Sample count times depend on the sample volume, geometry, and the client's required minimum detectable concentration (MDC). An outline of the geometries and their respective matrix and/or volume can be found in Appendix C of this SOP. LCS samples are typically counted for 1800 seconds (30 minutes) and blank samples will be counted for as long as the longest sample count time.

7.2.3 After the sample ID and count time have been entered and saved, clear the previous spectrum by selecting the 'ERASE' icon.

7.2.4 Begin spectrum acquisition by selecting the 'GO' icon and exit the 'TOOLS' window by selecting 'DONE'.

7.2.5 Enter all samples that are analyzed in the gamma spectroscopy logbook . Use the current page with the date that the sample is counted. *Ensure that the detectors being used have passed the Daily QC checks (see Section 8 below).* Necessary information recorded in the gamma spectroscopy logbook includes:

- ALS sample ID
- detector number
- geometry, including sample orientation and the use of a positioning (puck), if appropriate
- duration of the count
- count start time
- operator's initials
- spectrum file name
- position verification check

7.3 SPECTRUM ANALYSIS

Upon completion of the sample count, the data must be transferred to the workspace and analyzed, using the procedures described below:

7.3.1 Select the appropriate detector, then select the appropriate analysis/application type, based on the sample geometry, from the Application Select menu. Next select 'Read MCA' on the menu bar. By "reading the MCA", the data acquired during the analysis count is transferred to the workspace and default settings and files from the application are applied (i.e., efficiency, library, units, etc.).

When 'Read MCA' is selected, the analysis parameters screen is displayed. At this time the file name is automatically generated. Record this file name in the gamma spectroscopy run log.

The analyst will need to verify, enter, or edit the following sample parameters:

Sample ID: This should be automatically transferred in the format described above, but corrections can be made here.

Spec. Code: This field is left blank.

Sample Size: Enter the volume, weight, or number of filters as appropriate.

Units: This will be transferred automatically as a default, but can be changed as needed.

Sampling Start and Stop: This is normally the same date and time for both the start and stop. Enter the collection date of the sample in both boxes. The time of day is generally 12:00:00 for all samples.

Efficiency File: This line should be generated automatically by the computer and is in the form:

$$(D_{xx})(S_{GG}).EFF$$

where:

xx is the detector number

GG is the geometry of the sample.

If changing the efficiency file, make sure the detector of the efficiency file is for the detector the sample was counted on and that the efficiency file has not expired.

After all the parameters and values are satisfactory, select 'OK' to exit the 'Read MCA' window. By selecting 'OK', all of the parameters and values are saved under the file ID and can be retrieved later to further analyze. By selecting 'CANCEL', all of the parameters are lost and the file ID is not saved.

7.3.2 Next, the spectrum must be analyzed to identify peaks at the various energies. To do this, select 'PEAK SEARCH' on the menu bar and the software will apply the resolution calibration to the acquired spectrum to define peaks and peak height. This will prompt the next window, which allows the analyst to see all of the peaks identified, and the counts acquired for each peak.

The analyst shall review the peak search results to identify peak shifts, multiplets, etc. After the peak search results are considered to be satisfactory, select 'DONE' to exit the peak search results window.

7.3.3 To calculate activity concentrations, select the 'CALCULATE' icon under 'ACTIVITY' on the menu tool bar. This will prompt an activity report parameters window. Then perform the following:

Select the desired library to be used in the column labeled 'LIBRARY FILE'. Next select the background file to be used according to the detector and the count date. Background files are named so that the first two numbers correlate to the detector, the next two correlate to the month the background was counted, and the next two correlate to the day of the month. *Background files can be used for one week after counting (i.e. sample counts must be started before the day and time that the background calibrations were completed on the previous week.)*

The LSF File should remain as 'NONE'.

The 'RESULTS FILE' and the 'PRINTOUT FILE' should be the same as the .SPC file, except ending in .RES and .TXT, respectively.

Select 'OK' after the correct library and background have been selected and the Library Search Results window will be shown. This allows the analyst to review peaks that have been matched to specific peaks in the library.

To **finish the calculations**, select 'OK' to prompt the raw data printout. This window allows the analyst to review all of the parameters used in the analysis.

To **save the data**, select the 'SAVE' icon, which calls up the "SAVE" window. For general analyses the fields are automatically populated. The default values (yynnnnD##.RES) are accepted, except where multiple analyses of a spectrum are performed, as described below.

Select "SAVE" again to store the results in the defined .RES file.

Print the raw data by selecting the 'PRINTER' icon.

In some cases, reanalysis of the same spectrum may be required to apply different geometry calibrations or analytical libraries. To perform multiple analyses on the same spectrum, select "SPECTRUM" on the menu bar, then select "EDIT" and return to step 7.3.1, beginning with the "Efficiency File" specification, with the following exception:

Multiple analyses of a single spectrum require a unique identifier appended to the default file name (yynnnnD##**A**.RES, yynnnnD##**B**.RES, etc.). The unique file name must be defined prior to saving the .RES file, to **prevent overwriting previous files**.

8 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

Standards for Daily QC Checks need not be traceable to the National Institute for Standards and Technology (NIST). All Daily QC monitoring shall be recorded in the gamma spectroscopy run log . **QC parameters must meet the established limits defined in the instrument software.**

8.1 QC MONITORING

8.1.1 DAILY QC ENERGY CALIBRATION CHECKS

A daily QC check involves performing an energy calibration, as well as monitoring the detector resolution (FWHM) and efficiency. Each detector has a labeled calibration standard. Center the appropriate calibration standard on the corresponding detector. Count each daily check standard as described in the procedure above for 20 minutes using the sample ID "Daily Check".

When the count is complete, select 'DAILY CHECK' under the Application Select menu, then select 'Read MCA' to prompt the edit

parameters screen. Select 'OK', as the parameters should be the default.

On the menu bar select 'PEAK SEARCH' as described above, then select 'Q.C.', then 'DETECTOR'. The calibration parameters screen is then prompted. Make sure that the 'ENERGY' bullet is selected.

Select 'OK', choose 'MERGE PSR', then select 'CURVE FIT', then select 'SAVE'. This will save the energy calibration for that day. The program then compares the results of the energy recalibration to the Q.C. parameters (found in the Q.C. editor) established for the specified detector.

8.1.2 CORRECTIVE ACTION FOR DAILY QC FAILURES

If a detector is not within established control limits for any of the bounds tests, corrective action must be taken as follows:

- If one of the centroid exceeds the bounds test (e.g., 662keV), the peak location should be adjusted. This is done by placing a calibration source on the detector (preferably a Laboratory Control Sample, LCS) and starting the detector.

  Clear the current spectrum by typing 'F4' (Clear). The acquisition can then be started by typing 'F2'.

  Move the cursor to the appropriate centroid (e.g., 662keV) and check the actual location. The peak can be moved by adjusting the fine gain, located on the amplifier. *Note that it only requires a minute adjustment (one click) to move the peak three to five keV.* After the peak has been moved to the correct location, re-run the energy calibration.

- If the failure includes one of the other parameters (e.g., FWHM or efficiency), the daily QC can be re-run. If the QC fails for a second time, the detector is taken off-line and the lab Supervisor is contacted.

  NOTE: A pole-zero adjustment can be conducted in the case of a FWHM failure, using the following procedure:

  First, **attach a co-axial cable** from the "1 Meg" port associated with the vertical input on the oscilloscope to the "uni" output on the amplifier.

  Next, **set the scope settings** as follows:

  Volts/Div(Vertical) = 0.1

Polarity = DC

Trigger Selector = EXT(-)

Mode = DC

Triggering Level = 0

Stability = Preset

Time/Div = 20μs

Variable = Calibrated

Next, **place a source on the detector** and **adjust the signal** so that it is as close to the baseline as possible by using the 'PZ ADJ' dial found on the amplifier.

The energy calibration can now be run again. If any parameter still fails, tag the detector out of service (SOP 317) and notify the lab Supervisor.

All calibration operations must be recorded in the run log, including fine gain adjustments, bounds re-calculations with start and end dates, and calibration re-runs.

8.2 EFFICIENCY CALIBRATION PROCEDURES

Standards for efficiency calibrations shall be traceable to the National Institute for Standards and Technology (NIST). Standards will normally be of the mixed-gamma, multiple-energy type available from several commercial suppliers. The analysis systems shall be calibrated for each physical form of sample to be analyzed (e.g., water, soil, filter, etc.) at least annually. A FWHM calibration shall also be performed at least annually. Note that there is only one FWHM calibration per detector, and it is not geometry specific. Before starting an efficiency calibration, consult with a Senior Instrument Technician. Record all efficiency calibrations in the gamma spectroscopy run log .

8.2.1 SPECTRUM ACQUISITION

Place the calibration source for the appropriate geometry on the detector to be calibrated. The efficiency calibration will be initiated like that of a sample count. First, an internal workorder number must be obtained from the current non-client workorder notebook (located in the radium/strontium lab). Use this workorder number and follow the same procedure used to count a sample. Be sure to enter the appropriate dates and time for the calibration standard (2 hours and/or a duration long enough to acquire 10,000 cts/per energy line that will be used in the calibration). For calibrations where 10,000 cts/per energy line cannot be acquired, Supervisory approval is required.

8.2.2 SPECTRUM ANALYSIS

8.2.2.1 After the acquisition is complete, the MCA of the sample

spectrum should be read. In the edit parameters screen, enter the standard calibration origin date, and the appropriate volume/sample size. Select 'PEAK SEARCH', then 'CALIBRATE'. The types of calibrations prompted are: Energy, FWHM and Efficiency. Make sure that the 'EFFICIENCY' bullet is selected. The calibration parameters screen is prompted, at which time the operator must choose the appropriate calibration standard, aliquot size and the appropriate fit formula for the efficiency curve (exponential fit is used in most cases).

Select 'OK' to prompt the calibration workspace. Transfer the peak search results by selecting 'MERGE PSR', then 'CURVE FIT'. View the results of the calibration.

The % difference for the measured efficiency should be less than +/- 5% for all nuclides, but may be up to 10% with specific written approval from the instrument lab Supervisor. If the measured difference exceeds this criterion, the calibration will have to be redone. If efficiency limits are met, select 'OK', then 'SAVE', and then print the calibration.

This calibration should be done annually or when maintenance has been conducted on the detector.

8.2.2.2 If the observed efficiencies need to be adjusted to optimize the fit of the calibration curve, this may be done with the approval of the lab Supervisor. *Do not adjust the Cs-137 efficiency.* If the other efficiencies need to be adjusted, manually calculate the new efficiency, by either increasing or decreasing by a known percentage (usually 5 to 10%).

DO NOT MANUALLY ADJUST EFFICIENCIES WITHOUT FIRST CONFERRING WITH A SENIOR INSTRUMENT TECHNICIAN.

After adjusting a peak, re-start the calibration process (choose the print to screen option until the efficiencies have been accurately adjusted). Manual adjustments are conducted in the calibration work space.

In all cases, manual adjustments of peak efficiencies will be noted on the calibration output page.

8.2.2.3 After the calibration has been stored, analyze an LCS with the appropriate geometry for 1800 seconds to verify the calibration. This analysis must pass normal LCS

acceptance criteria.

8.3 ANALYZE INITIAL DAILY CHECK TO SET CONTROL LIMITS

8.3.1 Perform a daily check and set control limits off of observed values.

8.3.1.1 Centroid: ± 2 Channels

8.3.1.2 FWHM: ± 35%

8.3.1.3 Efficiency: ± 10%

8.4 FWHM CALIBRATION

8.4.1 Place a current calibration source on the detector (typically GEO 1 or GEO 13) and begin acquiring count data. The count time is dictated by the sample activity and achieving 10,000 counts in each energy line used to calibrate. The sample ID is the in-house work order number, detector number, calibration type and standard used (example: 0713001-1 FWHM CAL (824)).

8.4.2 After the count time is complete, ensure that the correct geometry is selected for sample analysis then READ MCA and enter standard reference date as sampling date start/end time. Reference time is 12:00 noon Eastern Standard Time adjust to 10:00 Mountain Standard Time.

8.4.3 Do a peak search on the data read from the MCA. Look for any peak shifts but more importantly peak fit errors (ie small peaks near analyte peaks of interest).

8.4.4 Select QC->FWHM from the tool bar. Make sure that the appropriate standard is selected for the standard file. Do not select a background subtraction file. Then select 'OK'.

8.4.5 Merge PSR and fit a curve. View Fit Results. The percent difference (% Diff) for all should be less than 10% for acceptance. Look at data points and curve fit for any points that are significantly out of line with other points. Select 'Done'.

8.4.6 Save FWHM calibration and print data report.

8.5 INITIAL BACKGROUND CALIBRATION

8.5.1 Perform a normal weekly background analysis. Set interim control limits off of observed values ± 10%.

8.6 WEEKLY BACKGROUND CALIBRATION

8.6.1 A background calibration is performed weekly. Use the general form,

"yymmdd-## Weekly Bkgd", for the sample ID.

8.6.2 Make sure there is no sample in the detector shield. Consult the gamma spec maintenance logbook to see if the detectors have been cleaned within the past month, if not, the detectors need to be cleaned per Section 8.3.5 below.

8.6.3 Start the counts for 1000 minutes (60000 seconds) for each detector in service. Geometry and aliquot are irrelevant.

8.6.4 Record detectors that have been started in the logbook. After the counts are complete, "Read the MCA" and do a 'PEAK SEARCH' as described above. At this point, review the acquired spectral data for evidence of peak-fit errors and/or gain shift. If the spectral quality is acceptable upon review of the 'PEAK SEARCH' results, save the background calibration by selecting 'SAVE AS BKGSUB'. Save each background file as DET##MMDD.BKG, where '##' is the detector number and 'MM' and 'DD' are the month and day the background was started. Then select 'BACKGROUND' under 'QC' on the menu bar. Select 'OK' to analyze the background and see if the count is within control limits. Record any failures in the run log, clean the detector (see 8.6.5 below), and restart the background calibrations.

8.6.5 WEEKLY CALIBRATION FAILURES
The inside of the detector must be thoroughly cleaned with a paper towel dampened with Radiacwash®, or an equivalent EDTA solution. Then wipe the detector with a paper towel dampened with DI water. Record the cleaning date in the gamma spec maintenance logbook.

After this has been done, the background calibration can be run again. If the detector fails after cleaning, the lab Supervisor must be notified and the detector must be tagged out of service (SOP 317) until the problem is resolved.

8.7 QC SAMPLES
One LCS and blank, per geometry, are to be analyzed with every batch of not more than 20 samples.

9. INTERPRETATION OF DATA

The spectrum analysis capabilities of the analytical software are only as good as the software set up. It is essential that appropriate analysis geometries, efficiency files, and library files be used to ensure accurate analyses. Results data must be reviewed as soon as it becomes available to ensure that the calibrations are correct, that the spectral quality is adequate, and that all Q.C. acceptance criteria have been met.
All unknown peaks greater than 5 times the listed critical level must be qualitatively identified on the raw data of the first sample for which they appear. The spectrum must also be reviewed to ensure that characteristic peaks, such as K-40 at 1460keV, and the annihilation peak at 511keV, do not show evidence of a gain shift. A gain shift may

show up as a secondary peak slightly offset from all the normal characteristic peaks in the spectrum. A spectrum that shows evidence of a gain shift must be rejected and the sample re-counted. The detector showing the gain shift must have the fine gain on the amplifier adjusted as described previously in Step 8.1.2.

10. PERIODIC MAINTENANCE

Each detector has a Dewar filled with liquid nitrogen to keep the germanium detector cold. Twice per week, the detector Dewars must be filled with liquid nitrogen. Allow 15 minutes after filling before resuming data acquisition.

If a Dewar runs out of liquid nitrogen between fillings, the red bias display, located on the 'BIAS SUPPLY' control board, will be shutdown. If this occurs, tag the detector out of service, and do not operate the detector until the Dewar can be re-filled. The detector may need to be cycled through ambient room temperature before being re-cooled. The lab Supervisor must be notified before proceeding.

To fill the Dewar, follow the steps below:

- We use the vertical cryostat mounting arrangement; if liquid nitrogen (LN_2) or cold vapor contacts the top section of the detector the pre-amplifier may malfunction (due to heating and cooling or moisture) and/or the vacuum seal may be breached.
  - É Care must be taken to ensure that LN2 does not contact the cryostat, endcap of electronics section of the detector system.
  - É Filling the dewar-flask slowly helps to avoid detector contact between LN2 and cold vapors. The valve on the LN2 source can be opened full and the second valve used to control flow.
- Dewar Flange/Silicone Collar: The silicone collar contains two tubes used for gas fill and exhaust. The exhaust tube prevents the LN_2 level from rising to within 6 inches of the dewar flange if there are no leaks at the collar. **It is important not to damage the silicone rubber collar**. Do not use excessive force to attach or remove a hose from the fill tubes.
- Stop immediately when the dewar is full.
- Safety: Relieve pressure at supply dewar and allow hoses to thaw completely before removing.

If detector is being cooled from ambient temperature, manufacturer recommends overnight equilibration./SI 21Mar07

- Record all liquid nitrogen fills and re-fills in the gamma LN2 fill logbook.

11. DEVIATIONS FROM THE METHODS

Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ±20%, irrespective of the lab's internally derived acceptance criteria.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.3 SAFETY AND HAZARDS

All Safety and Hazards are managed in accordance with the current facility plans:

- Chemical Hygiene Plan (CHP)
- Radiation Protection Plan (RPP).
- Emergency and Contingency Plan (ECP)
- Respiratory Protection Plan (RESPP)

12.4 WASTE DISPOSAL
All Wastes are disposed of in accordance with the Waste Management Plan (WMP)

13. REFERENCES

13.3 ANSI N42.14, American National Standards Institute, Calibration and Usage of Germanium Detectors for Measurement of Gamma Ray Emission of Radionuclides, April 1978, Reaffirmed April 1985.

13.4 EPA-600/4-80-032, Prescribed Procedures for Measurement of Radioactivity in Drinking Water, "Method 901.1, Gamma Emitting Radionuclides", August 1980.

APPENDIX A
COMMON GAMMA ENERGIES AND CHANNEL LOCATIONS

This Section is provided to assist in determining proper channel locations during calibrations and QC checks.

NUCLIDE	*ENERGY (keV)	TARGET CHANNEL
Am-241	59.54	120
Cd-109	88.04	176
Co-57	122.06	244
Cs-137	661.65	1324
Y-88	898.04	1796
Co-60	1173.22	2346
Co-60	1332.49	2664
Y-88	1836.06	3672

* The Kocher's Decay Manual is the primary source (located on the network at work order review) used for determining the energy lines of the gamma photons used in the gamma spectroscopy libraries. Some libraries are set-up according to client specified energy lines in which case the source is unknown.

NOTE: ALS uses a 2.0keV matching tolerance for nuclide/energy matching; this will allow up to a 4 channel deviation from target channels. In addition, the daily QC checks perform energy versus channel calibrations each time they are run, correcting for small changes in peak channel locations.

APPENDIX B
GEOMETRY/EFFICIENCY LIST

Geometry Number	Geometry Description	Default Count Time (min.)	Efficiency file/Standard file number
01	1 liter H_2O in 2 liter Marinelli	300	01
07	47mm Filter	60	07
08	Five 10 cm filters	1000	08
09	Hi-Q charcoal cartridge	60	09
13	500g Solid	30	13
11	100g Solid	30	11
*17	215g Solid	30	17
18	1350g Solid	120	18
*26	215g Solid (Ra-226)	30	26
27	1332g Solid (Ra-226)	120	27

* Unless otherwise directed, samples packed for Geo17/26 will be ingrown 21 days before analysis to allow Rn-222 to approach secular equilibrium with its parent, Ra-226.

APPENDIX C

SUMMARY OF INTERNAL QUALITY CONTROL (QC) PROCEDURES AND CORRECTIVE ACTION

QC Check	Frequency	Acceptance Criteria	Corrective Action
Efficiency Check	Daily	Within derived control limits, as established in instrument software.	Recount, re-evaluate, service instrument, if necessary or document why condition is acceptable.
Peak Resolution Check	Daily	Within derived control limits, as established in instrument software.	Recount, re-evaluate, perform pole-zero adjustment, if necessary, and repeat daily performance checks.
Energy Calibration	Daily	Within derived control limits, as established in instrument software.	Recount, re-evaluate, perform fine gain adjustment, if necessary, and repeat daily performance checks.
Peak Background Calibration	Weekly	Within derived control limits, as established in instrument software.	Clean detector, recount, re-evaluate, or document why condition is acceptable.
Efficiency Calibration	Yearly, for each counting geometry.	Each fitted value is within 5% of the observed value. Subsequent LCSs pass within normal acceptance criteria. *	Tag geometry off-line. Determine and correct problem; verify source activity; recount and/or recalibrate. With supervisors written approval, fitted values may be within 10% of observed value.
Peak Resolution (FWHM) Calibration	Yearly	Each fitted value is within 10% of the observed value. Subsequent LCSs pass within normal acceptance criteria. *	Perform pole-zero adjustment, if necessary, and repeat.
Gain shift	Each sample	Review each spectrum to ensure that characteristic peaks @ 511, 1460 KeV are present, not shifted during the count, and properly ID'd by software.	Recount sample after daily performance checks are successfully performed.

NOTE: This SOP and SOP 715 contain acceptance criteria and corrective action for method blank, laboratory control samples, duplicate samples and matrix spike/matrix spike duplicates.

* as established in the applicable LIMS nickname (e.g., Paragon Standard or as created for a specific client

APPENDIX D

GENERAL GAMMA DETECTOR INTALLATION NOTES

Upon receipt of a new or repaired detector the following steps must be taken prior to data acquisition.

1) Inspect the detector for damage during transit.
2) Review accompanying documentation to ensue the following;
    a. Quality Assurance Data Sheet. This documents the detector performance after repair/manufacture.
    b. Spectrum Printout: Supplements the QADS.
    c. Repair Analysis Report (if detector was repaired). This documents the problems identified with the detector and any corrective action/repairs that were undertaken.
3) Cool the detector.

NOTE: The detector must be cooled overnight before applying bias. Do not connect the detector cabling until the assembly has cooled in LN overnight.

a. Inspect the nitrogen dewar to be used, if necessary.

    Note: In all cases, the dewar should not be placed directly on the floor. Insert some vibration absorbing material between the dewar and the floor to minimize microphonic noise (low frequency harmonics) in the detector.

b. Fill the dewar with LN, to within 3-4" of the top of the neck. Do not allow the LN to overflow or to contact the latex collar, though the collar will be cold after filling.
c. Allow the collar to warm for 20-30 minutes to allow enough flexibility to insert the detector cryostat.
d. At this step it is helpful to have a second technician waiting underneath the shield to receive the detector cables and to adjust the position of the dewar, as necessary.
e. Feed the long grey pre-amp cable through the top of the opening in the shield.
f. Carefully insert the cryostat through the shield, into the LN dewar. After inserting the cryostat partway, feed the detector leads through the opening. It may be necessary to move the dewar slightly to one side to accomplish this.
g. After all the cables are clear of the shield and collar, center the dewar and insert the cryostat completely into the LN.
h. The initial cooling of the detector may use a significant volume of LN. After the detector has cooled for 2-3 hours, top off the LN, filling the dewar until the LN spills out of the overflow port.

APPENDIX E

EXAMPLE

Gamma Spectrometer Calibration Log

Daily checks are run for 10 minutes on each currently operating detector. Each detector has an individual check source prepared from a dilution of standard #6635A-307, #68681-307 and #64122-307.

ALS

Gamma Spectrometer Calibration Log

Date: _____ Reviewed By/Date: _____

Det. No.	Out Of Service	Background		Source Check			Repeat Source Check			
		Started	OK	Started	OK	Failed Parameter(s)	OK	Failed Parameter(s)	Corrective Action Taken **	Removed from Service
1.										
2.										
3.										
4.										
5.										
6.										
7.										
8.										
9.										
10.										

.** **Corrective Action:**

_____ **A** ***ALS***

Gamma Spectrometer Run Log

Date: _____ Reviewed By/Date: _____

CONFIDENTIAL

Sample ID	Ver[1]	Det. No.	Geo[2]	Count Dur. (min.) [3]	Start Time	Analyst	File ID/Comments	Saved?

[1] Analyst will verify the position, detector, and geometry when the sample is removed from the detector.

[2] Calibration geometry.

[3] Count duration.

KEY: * sample was counted on a puck
↑ sample was counted with air flow arrow pointing up
↓ sample was counted with air flow arrow pointing down

_____ **B**

CONFIDENTIAL

Appendix C

Data Validation Standard Operating Procedures

Validation SOP
No. V-1

EDS SOP, HCX Rev. 0, 8/11

Environmental Data Services
Validation Guidelines for Hexachloroxanthene

SITE:
DATE:
SDG:
VALIDATOR:

All deliverables must be clearly labeled with the associated sample number. Review the data package to assure that all items listed below are provided. Missing, illegible or incorrectly labeled items must be checked off. The laboratory should immediately be contacted and requested to submit the missing or incorrect items.

	Y	N	N/A
Data Completeness and Deliverables			
Are the Reports and Forms present for all samples?			
Traffic Report	_____	_____	_____
Field Chain of Custody	_____	_____	_____
Laboratory Chain of Custody Records	_____	_____	_____
Sample Shipment Records	_____	_____	_____
% Solid Worksheet	_____	_____	_____
Are the Case Narrative and Cover Letter present?	_____	_____	_____
Do the Field Chain of Custody Reports or Lab Case Narrative indicate problems with sample receipt, sample condition, analytical procedures, or other comments regarding the quality of the data?	_____	_____	_____

ACTION: Use professional judgment to evaluate the effect of the noted problems on the quality of the data.

ACTION: If any solid sample analyzed contains 50% to 90% water, all data shall be flagged as estimated "J". If a solid sample contains more than 90% water, then qualify positive hits "J" and non-detects "R".

Reporting Requirements and Deliverables			
Are the following forms present?			
Sample Data Summary	_____	_____	_____
Initial Calibration Summary	_____	_____	_____
Initial Calibration Ion Ratio Summary	_____	_____	_____
Routine Calibration Summary	_____	_____	_____
A Chronological List of All Sample Analyses	_____	_____	_____
Matrix Spike/Matrix Spike Duplicate Summary	_____	_____	_____
Method Blank Summary	_____	_____	_____

	Y	N	N/A

GC/MS Displays

Are the following GC/MS Displays present?

Standard and sample chromatograms. SICPs list date and time of analysis; the file name; sample number; and instrument I.D. number	_____	_____	_____
Integrated area and peak height must be listed for all peaks 2.5 times above background	_____	_____	_____
SICP for the initial calibration standard	_____	_____	_____
SICP for the continuing calibration standard	_____	_____	_____
SICP for each sample run	_____	_____	_____

Laboratory Records

GC/MS Standard and Sample Run Log in chronological order	_____	_____	_____
Sample Extraction Log	_____	_____	_____

ACTION: If deliverables are missing call the lab for explanation/ resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the reviewers narrative.

Holding Times

Have any holding times been exceeded for:

aqueous samples 14 days from sample collection to extraction	_____	_____	_____
soil/sediment samples 14 days from sample collection to extraction	_____	_____	_____
all samples 40 days from time of extraction to time of analysis	_____	_____	_____

ACTION: If holding times are exceeded, flag all data as estimated "J". If holding times from collection to extraction, or from extraction to analysis have been grossly exceeded, use professional judgment to determine whether non-detects shall be rejected.

Preservation Requirements

Is the cooler temperature ≤ 10°C for aqueous and soil samples from the time of collection until receipt at the laboratory?	_____	_____	_____

ACTION: If cooler temperature >10°C, flag non-detects as "UJ" and detects as "J".

	Y	N	N/A

Instrument Performance

Mass Calibration - Mass calibration of the MS must be performed prior to analyzing calibration solutions, blanks, samples, and QC samples. A static resolving power of at least 10,000 (10% valley definition) must be demonstrated at appropriate masses before any analysis is performed at appropriate masses. Include in the narrative, minimum required resolving power of 10000 was obtained for perfluorokerosene (PFK) ion 380.9760. This is done by first measuring peak width at 5% of the maximum. This should not exceed 100 ppm, i.e., it should not exceed 0.038, for ion 380.9760. Resolving power, then is calculated using the formula,

Resolving Power = m/_m = 380.9760/0.038 = 10025

Was mass calibration performed at the frequency given above? _____ _____ _____

Initial 5-Point Calibration

The initial calibration standard solutions (CS0 - CS6) must be analyzed prior to any sample analysis. However, initial calibration should be analyzed whenever a new set of standards are created and/or continuing calibration falls outside the acceptance criteria. The calibration standards must be analyzed on the same instrument using the same GC/MS conditions that are used to analyze the samples.

The following MS/DS conditions must be used:

Is mass calibration performed as described earlier _____ _____ _____

Is the total scanning time $\leq$ 1 second _____ _____ _____

Were SIM data acquired for each:

Native HCX ions: 387.84 and 389.83 _____ _____ _____

Internal Standard ions: $^{13}C_{12}$-1,2,3,7,8,9-HxCDF 383.86 and 385.86 _____ _____ _____

Recovery Standard ions: $^{13}C_{12}$-1,2,3,4,6,9-HxCDF 383.86 and 385.86 _____ _____ _____

Were the following GC criteria met:

The absolute retention times of internal standard, $^{13}C_{12}$-1,2,3,7,8,9-HxCDF, recovery standard $^{13}C_{12}$-1,2,3,4,6,9-HxCDF and native HCX shall not change by more than 10 seconds between the ICC3 analysis and the analysis of any other standard. _____ _____ _____

	Y	N	N/A
The relative ion abundance criteria for HCX and standards listed in Table 1A and 1B (see analytical method) must be met.	_____	_____	_____
For all calibration solutions, the signal to noise ratio (S/N) for the GC signal present in every SICP, including the ones for the labeled standards must be $\geq$ 10.	_____	_____	_____
The percent relative standard deviations (%RSD) for the mean Response factors (RRF) from the initial calibration for unlabeled standards must not exceed $\pm$ 20%.	_____	_____	_____

ACTION: 1) If the %RSD for any isomer exceeds 20%, flag the associated sample positive results for that specific isomer as estimated ("J"). No effect on the non-detect data.

2) If the ion abundance ratio for an analyte is outside the limits flag the results for that analyte R (reject).

3) If the ion abundance ratio for the internal standard falls outside the QC limits flag the associated positive hits with J. No effect on the non-detects.

4) If the signal to noise ratio (S/N) is below control limits, use professional judgement to determine quality of the data.

5) If the selected monitoring ions specified in Table 1A and 1B were not used for data acquisition, the lab must be asked for an explanation. If an incorrect ion was used, reject all the associated data.

6) If mass calibration criteria as specified earlier is not met, specify that in narrative notes.

7) Non-compliance of all other criteria specified above should be evaluated using professional judgement.

Spot check relative response factor (RRF) calculations and ion ratios. Ensure that the correct quantitation ions for the unlabeled HCX and labeled internal standard and recovery standard were used. In addition verify that the appropriate labeled compound was used.

Y N N/A

To recalculate the RRFs for the Initial Calibration:

For HCX, labeled internal standard compound and recovery standard listed in Table 1A and 1B:

$$RRF_i = \frac{(A_{n1} + A_{n2}) \times Q_{is}}{(A_{is1} + A_{is2}) \times Q_n}$$

Where:

$A_{n1} + A_{n2}$ = The integrated areas of the primary and secondary ions of isomer of interest, HCX

$A_{is1} + A_{is2}$ = The integrated areas of the primary and secondary ions of the appropriate internal standard, $^{13}C_{12}$-1,2,3,7,8,9-HxCDF

Q_{is} = quantity of the appropriate labeled internal standard, $^{13}C_{12}$1,2,3,7,8,9-HxCDF injected (pg)

Q_n = quantity of the unlabeled HCX analyte injected (pg)

Continuing Calibration (HRCC3)

The continuing calibration must be performed at the beginning of a 12 hour period after successful mass resolution and GC resolution performance checks.

Was the continuing calibration run at the required frequency? _____ _____ _____

Was the following MS/DS conditions met:

The total scanning time was ≤1 second. _____ _____ _____

ACTION: If the requirement is not met, use professional judgement to determine the validity of the data.

Were SIM data acquired for each:

Native HCX ions: 387.84 and 389.83 _____ _____ _____

Internal Standard ions: $^{13}C_{12}$-1,2,3,7,8,9-HxCDF 383.86 and 385.86 _____ _____ _____

Recovery Standard ions: $^{13}C_{12}$-1,2,3,4,6,9-HxCDF 383.86 and 385.86 _____ _____ _____

	Y	N	N/A
Was following GC criteria must be met:			
The absolute retention time of the internal standards $^{13}C_{12}$1,2,3,4,6,9-HxCDF and $^{13}C_{12}$-1,2,3,7,8,9-HxCDF as well as HCX shall not change by more than 15 seconds between the initial HRCC3 and ending HRCC3 standard analyses.	____	____	____
The %D for the native HCX should fall in the acceptance criteria (70-130%)	____	____	____
The %D for the internal standards should fall in the acceptance criteria (50-150%)	____	____	____
ACTION: When the %D for either native HCX or the internal standards are outside criteria, all data are flagged "J" or "UJ" as appropriate.			
Was the same internal standard compound used to calculate RRF for HCX the initial calibration?	____	____	____
ACTION: If any of these requirements are not met, use professional judgement to determine the validity of the data.			
The two SIM ions for each homolog must maximize simultaneously ± 2 seconds .	____	____	____
For the CC3 standard solution, the signal to noise ratio (S/N) for the unlabeled HCX ion shall be greater than 10.	____	____	____
For the labeled internal standards, $^{13}C_{12}$1,2,3,7,8,9-HxCDF and the recovery standard $^{13}C_{12}$-1,2,3,4,6,9-HxCDF the signal to noise ratio (S/N) shall be greater than 10.	____	____	____
The relative ion abundance criteria (Table 1A - analytical method) for HCX shall be met.	____	____	____
The relative ion abundance criteria for the internal standard and recovery standard (Table 1B - analytical method) must be met.	____	____	____
ACTION: If any of these requirements are not met reject all data (flag R) directly affected by each specific problem.			
The found concentration for each analyte must fall within the concentration range established by the initial calibration.	____	____	____
ACTION: When the found concentration of the calibration verification sample falls outside the specified allowable range, all data for outlier congeners are flagged J.			
ACTION: If the continuing calibration standard was not analyzed at the required frequency, reject all the data.			

Spot check relative response factor (RRF) calculations and ion ratios. Verify that the appropriate quantitation ions for the HCX, internal standard and recovery standard were used.

Y N N/A

To recalculate RRFs for HCX, and the RRFs for the internal and recovery standard use the following equations:

$$RRF_n = \frac{(A_{n^1} + A_{n^2}) \times Q_{is}}{(A_{is^1} + A_{is^2}) \times Q_n}$$

$$RRF_{is} = \frac{(A_{is^1} + A_{is^2}) \times Q_{rs}}{(A_{rs}^{1} + A_{rs^2}) \times Q_{is}}$$

Where:

$A_{n1} + A_{n2}$ = The sum of the areas of the primary and secondary m/z's for the analytes of interest, HCX.

$A_{is1} + A_{is2}$ = The sum of the areas of the primary and secondary m/z's for the internal standard, $^{13}C_{12}$-1,2,3,7,8,9-HxCDF

$A_{rs1} + A_{rs2}$ = The sum of the areas of the primary and secondary m/z's for the recovery standard, $^{13}C_{12}$-1,2,3,4,6,9-HxCDF

Q_{is} = quantity of the appropriate labeled internal standard, $^{13}C_{12}$-1,2,3,7,8,9-HxCDF, injected (pg)

Q_n = quantity of the unlabeled HCX analyte injected (pg)

Q_{rs} = quantity of the labeled recovery standard, $^{13}C_{12}$-1,2,3,4,6,9-HxCDF

RRF_n = Relative response factor from the continuing calibration

To calculate percent difference use the following equation:

$$\% \text{ Difference} = \frac{(RRFi - RRF_n) \times 100}{RRFi}$$

Where:

RRF_i = Relative response factor established during initial calibration.

RRF_n = Relative response factor established during continuing calibration.

Sample Data

The following MS/DS conditions were used:

Scanning time was ≤1 second. _____ _____ _____

SIM data were acquired for each of the ions listed in Table 1A and 1B (see analytical method) _____ _____ _____

Identification Criteria

		Y	N	N/A
B.	The absolute retention time for HCX must be within +/-2 percent of the labeled internal standard, $^{13}C_{12}$-1,2,3,7,8,9-HxCDF.	____	____	____
	ACTION: Reject (R) all positive data for the HCX compound.			
	The integrated ion current for each characteristic ion of the HCX analyte must be at least 2.5 times background noise and must have not saturated the detector.	____	____	____
	ACTION: If the integrated ion HCX criteria is not at least 2.5 times background and the detector is saturated but all other criteria are met, qualify all positive data of the specific analyte with J.			
	The integrated ion current for the labeled internal standard compounds characteristic ions must be at least 10 times background noise.	____	____	____
	ACTION: If the integrated ion current for the internal standard ion characteristics are not met but all other requirements are met qualify the positive data of the corresponding analytes with "J".			
	The relative ion abundance criteria (Table 1A - analytical method) for all HCX found present must be met.	____	____	____
	ACTION: If the HCX reported positive do not meet ion abundance criteria, reject (R) all positive data for this analyte. Change the positive values to EMPC (estimated maximum possible concentration).			
	The relative ion abundance criteria for the labeled internal standard and recovery standard must be met (Table 1B - analytical method).	____	____	____
	ACTION: If labeled internal standards $^{13}C_{12}$-1,2,3,7,8,9-HxCDF and recovery standard $^{13}C_{12}$-1,2,3,4,6,9-HxCDF do not meet ion abundance criteria (Table 1B - analytical method) but they meet all other criteria flag all corresponding data with "J".			
	The identification of a GC peak as a PCDF can only be made if no signal having a S/N $\geq$ 2.5 is detected at the same time in the corresponding polychlorinated diphenyl ether channel. Is the above condition met?	____	____	____
	The HCX concentration must be within the calibration range. If not, dilution should have been made to bring the concentration within the calibration range. Was the above criteria met?	____	____	____
	ACTION: Flag HCX results that are not within the calibration range “J” estimated.			
	Do any lock mass ion signals show peak deflections of greater than 50% in the retention time areas of any analyte?	____	____	____

Y N N/A

ACTION: If any peak deflection is greater than 50%, then qualify the associated compound with a "J".

Spot check calculations for positive data and verify that the same labeled internal standards used to calculate RRFs were used to calculate concentration and EMPC.

To recalculate the concentration of individual HCX isomers in the sample use the following equation:

ALL MATRICES OTHER THAN WATER

$$Cn\ (pg/g) = \frac{(A_{n1} + A_{n2}) \times Q_{is}}{W \times (A_{is1} + A_{is2}) \times RRF_n}$$

WATER

$$Cn\ (pg/L) = \frac{(A_{n1} + A_{n2}) \times Q_1}{V \times (A_{is1} + A_{is2}) \times RRF_n}$$

Where:

A_{n^1} and A_{n^2} = The sum of the areas of the primary and secondary m/z's for the analye of interest, HCX.

A_{is^1} and A_{is^2} = The sum of the areas of the primary and secondary m/z's for the Internal standard, $^{13}C_{12}$-1,2,3,7,8,9-HxCDF

Cn = concentration of analyte (pg/g, pg/L)
W = Weight (g) of sample extracted
V = Volume (ml) of sample extracted
Q_{is} = Quantity (pg) of the appropriate labeled internal standard ($^{13}C_{12}$-1,2,3,7,8,9-HxCDF) compound added to the sample prior to extraction.
RRF_n = Calculated relative response factor from continuing calibration for the analyte HCX.

Estimated Detection Limits (EDL)

Was an EDL calculated for each HCX that was not identified _____ _____ _____

Use the equation below to check EDL calculations:

ALL MATRICES OTHER THAN WATER

$$EDL\ (pg/g) = \frac{2.5 \times Q_{is} \times H_{x^1} \times D}{W \times H_{is^1} \times RRFn}$$

WATER

$$EDL\ (pg/L) = \frac{2.5 \times Q_{is} \times H_{x^1} \times D}{V \times H_{is^1} \times RRFn}$$

Y N N/A

Where:

$H_{x'}$ = peak height of the noise for the ion of the analyte of interest, HCX

V = Volume of the sample (ml)

W = Weight of the sample (g)

$H_{is'}$ = peak height of the quantitation ion of the internal standard, $^{13}C_{12}$-1,2,3,7,8,9-HxCDF

RRFn = Calculated relative response factor for the analyte

D = dilution factor

Q_{is} = Quantity (pg) of the internal standard added to the sample before extraction.

NOTE: The validator should check the EDL data to verify that peak heights and not areas were used for this calculation. If the area algorithm was used, the validator should contact the laboratory for recalculation.

Estimated Maximum Possible Concentration (EMPC)

Was an EMPC calculated for HCX that had S/N ratio for the quantitation and confirmation ions greater than 2.5, but did not meet all the identification criteria? ____ ____ ____

Use the equation below to check the EMPC calculations:

ALL MATRICES OTHER THAN WATER

$$EMPC\ (pg/g) = \frac{(A_{n1} + A_{n2}) \times Q_{is} \times D}{W \times (A_{is1} + A_{is2}) \times RRFn}$$

WATER

$$EMPC\ (pg/L) = \frac{(A_{n1} + A_{n2}) \times Q_{is} \times D}{V \times (A_{is1} + A_{is2}) \times RRFn}$$

NOTE: See previous sections for definitions

ACTION: If the spot check calculations yielded EDLs or EMPCs different from those reported in Form I, contact the laboratory for an explanation.

	Y	N	N/A
Method Blanks			
Has a method blank per matrix been extracted and analyzed with each batch of 20 samples	____	____	____
If samples of same matrix were analyzed in different events (i.e. different shifts or days) has one blank for each matrix been extracted and analyzed for each event	____	____	____

ACTION: If the proper number of method blanks were not analyzed, notify the contractor. If they are unavailable, reject all positive sample data. However, the reviewer may also use professional judgement to accept or reject positive sample data if no blank was run.

Native Hexachloroxanthene levels measured in the method blank must be less than the quantitation limit or five times lower than the concentration found in any sample within the analytical batch.

Was HCX found at a concentration greater than the PQL in the associated method blank	____	____	____
If yes, has the method blank and associated samples been re-extracted	____	____	____

ACTION: If no, prepare a list of samples associated with each of the contaminated method blank(s) which have not been re-extracted

ACTION: If the concentration of HCX in the sample is < than 5 times the concentration in the blank, qualify the data as a non-detect “U”.

ACTION: If the concentration of the HCX in the sample is > than 5 times the concentration in the blank, no action is needed.

Rinsate Blank			
One rinsate blank must be collected for each batch of 20 soil samples or one per day whichever is more frequent.	____	____	____
Do any rinsate blanks show the presence of HCX that is >PQL	____	____	____

ACTION: If any rinsate blank was found to be contaminated with any of the HCX document in case narratives.

	Y	N	N/A

Ongoing Precision and Recovery (OPR)

The laboratory must analyze an OPR after the analysis of the calibration verification and before the analysis of any sample in each set.

Was the OPR standard analyzed at the required frequency _____ _____ _____

Did the OPR standard pass the concentration criteria limits:

HCX - (50-150%) _____ _____ _____

^{13}C-1,2,3,7,8,9-HxCDF (30-140%) _____ _____ _____

NOTE: If the OPR of an isomer is outside the recommended control limits and the internal standard recovery of that isomer in the associated samples is also out of range, than the sample and the OPR should be re-extracted and analyzed.

ACTION: If the criteria has not been met, contact the laboratory. If a decision is made to continue with validation, all data at a minimum should be qualified as estimated "J".

Initial Precision and Recovery (IPR)

Was an initial precision and accuracy demonstration performed for the appropriate matrix as per method _____ _____ _____

Were the results of the IPR evaluation acceptance when compared to the acceptance limits in Method1668A _____ _____ _____

ACTION: If IPR date was not provided by the laboratory, contact the lab to obtain the results of the IPR study.

ACTION: If the results of the laboratories IPR study do not meet the acceptance criteria for performance tests based on criteria in Method 1668A contact the lab to initiate remediation of technical difficulties.

Internal Standard Recovery

Were the samples spiked with the labeled internal standard, $^{13}C_{12}$-1,2,3,7,8,9-HxCDF compound as specified in the method? _____ _____ _____

Was the labeled internal standard compound recovery within the required (25-150%) limits? _____ _____ _____

	Y	N	N/A
If not, were samples reanalyzed?	_____	_____	_____

ACTION: If the labeled internal standard recovery was below 25 percent, reject (R) all associated non-detect data (EMPC/EDL) and flag with "J" all positive data.

ACTION: If the labeled internal standard recovery is above the upper limit (150 percent) flag all associated data (positive and non-detect data) with "J".

ACTION: If the labeled internal standard recovery is less than 10% qualify all associated data R (Reject).

Calculate the percent recovery of labeled internal standard compound (Ris) in the sample extract using the following equation.

$$\%\,\mathrm{Recovery} = \frac{(A_{is1} + A_{is2})(C_{rs})}{(A_{rs1} + A_{rs2})(C_{is})(RRF)}\,x\,100$$

Where:

$A_{is1} + A_{is2}$	=	The integrated areas of the primary and secondary m/z's for the internal standard $^{13}C_{12}$-1,2,3,7,8,9-HxCDF
$A_{rs1} + A_{rs2}$	=	The integrated areas of the primary and secondary m/z's for the internal standard $^{13}C_{12}$-1,2,3,4,6,9-HxCDF
C_{is}	=	The concentration of the internal standard
C_{rs}	=	The concentration of the recovery standard
RRF_n	=	Calculated Relative Response Factor for the analyte.

	Y	N	N/A

Internal Standards

There are no contractual criteria for the Internal Standard area. However, because it is very critical in determining instrument sensitivity, the internal standard area must be checked for every sample.

Are the internal standard areas for every sample and blank within the upper and lower limits of each associated ICC3? _____ _____ _____

Area upper limit = +100% of recovery standard area.
Area lower limit = - 50% of recovery standard area.

Is the retention time of each internal standard within 10 seconds of the associated ICC3? _____ _____ _____

ACTION: If the internal standard area is outside the upper or lower limits flag all related positive and non-detect data (EMPC/EDL) with "J" regardless whether the labeled analog compound recoveries met specifications or not.

If extremely low area counts (<25%) are reported flag all associated non-detect data as unusable (R) and the positive data J.

If the retention time of the internal standard differs by more than 10 seconds from the ICC3 use professional judgement to determine the effect on the results. A time shift of more than 10 seconds may cause certain analytes to elute outside the retention time window by the GC column performance check solution.

Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Sample ID of the sample chosen for MS/MSD analysis: _____

For every sample delivery group of 20 or fewer environmental samples was one MS/MSD pair analyzed _____ _____ _____

Is the MS recovery within the 50 to 150% acceptance range _____ _____ _____

ACTION: If the recovery is out of the 50-150% range and the sample concentration is less than four times the spike concentration, qualify as estimated "J", the analyte in the sample used for MS/MSD.

Does the precision of the MS/MSD analyses meet the $\leq$ 20% RPD criteria _____ _____ _____

ACTION: Qualify the value for that analyte in the sample used for the MS/MSD as estimated "J"; use professional judgment in association with signal to noise ratios and internal standard recoveries for the associated sample data to determine the effect on the quality of the associated sample data.

	Y	N	N/A
Field Duplicate Subsamples			
Sample IDs of the field duplicate pair: _____			
For every batch of 20 samples or less collected there must be a sample designated as duplicate.	_____	_____	_____
For Soil: RPD ≤ 50% when target is detected in both field duplicate samples at ≥ 5x PQL, or concentration differs by less than 2x the PQL when detects are < 5x PQL for both field duplicate samples.			

Data Validation Qualifiers

Qualifier	Description
J	Estimated value (bias undetermined) – The analyte was positively identified; but the associated numerical value is the approximate concentration of the analyte in the sample.
UJ	Estimated non-detect - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
M	The analytical result reported was obtained from a sediment sample found to contain between 50 and 90 percent moisture and had no other data qualifiers added during the data validating process.
EMPC	Estimated Maximum Possible Concentration (EMPC).
R	The sample results are rejected. Due to a significant QA/QC problem, the analysis is invalid and provides no information as to whether the analyte is present or not.

Validation SOP
No. V-2

USEPA Region 2 SOP HW-25,
Rev. 3

SOP HW-25
Revision 3
September 2006

USEPA REGION II DATA VALIDATION SOP FOR EPA METHOD 1613, REVISION B

Tetra- through Octa-chlorinated Dioxins and Furans by Isotope Dilution (HRGC/HRMS)

PREPARED BY: George Karras DATE: 12/05/06
George Karras, Chemist HWSS

PEER REVIEWED BY: Russell Arnone DATE: 12/05/06
Russell Arnone, Chemist HWSS
Hazardous Waste Support Section

CONCURRED BY: Linda Mauel DATE: 12/5/06
Linda Mauel, Chief HWSS
Hazardous Waste Support Section

APPROVED BY: [signature] DATE: 12/6/06
Robert Runyon, Chief
Hazardous Waste Support Branch

Annual Review Russell Arnone 08/11/09

Reviewed by: George Karras DATE: 12/30/08
Name

Reviewed by: _____ DATE: _____
Name

TABLE OF CONTENTS

Optional Quality Control and Assurance Requirements for Validation

1.0 Introduction

This method **was developed by the Engineering and Analysis division within the USEPA's Office of Science and Technology.** The method is used **for isomer specific determination** to detect the Tetra- through octa- chlorinated dibenzo-p-dioxins and dibenzofurans associated with the Clean Water Act (CWA, as amended 1987); the Resource Conservation and Recovery Act (RECRA, as amended 1986); **the Comprehensive Environmental Response,** the Compensation and Liability Act (as amended in 1986); **and the Safe Drinking Water Act** and other dioxin and furan compounds amenable to this method.

The dioxins and furans may be determined in water, soil, **sediment,** sludge, **tissue,** and other matrices using this method. The method is based on EPA, industry, and academic methods.

2.0 Applicability

The attached Standard Operating Procedure (SOP) is applicable to chlorinated dibenzodioxin and chlorinated dibenzofuran (CDD/CDF) data obtained using EPA Method **1613B,** Polychlorinated Dibenzodioxins (CDDs) and Polychlorinated Dibenzofurans (PCDFs) by Isotope Dilution using High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), **October 1994.** Its scope is to facilitate the data validation process of the data reported by the contracting laboratory and to ensure that the data is being reviewed in a uniform manner. This SOP is based upon the quality control and quality assurance requirements specified in Method **1613B, October 1994.**

3.0 Responsibilities/Scope

3.1 The reviewer must be knowledgeable of the analytical method and its QC Criteria.

3.2 The reviewer must complete the following:

3.2.1 Data Assessment Checklist - The data reviewer must read each item carefully and must check yes if there is compliance, no if there is non compliance and N/A if the question is not applicable to the data.

3.2.2 Data Assessment Narrative - The data reviewer must present professional judgement and must express concerns and comments on the validity of the overall data package. The reviewer must explain the reasons for rejecting and/or qualifying the data. Example of Data Assessment format is provided in Attachment A.

3.2.3 **Communication** Record Log - All **communication must be in writing, and it** must be documented on the **Communication** Record Log Sheet. A photocopy of the **Communication** Record Log is attached to the Data Assessment package.

3.2.4 Paperwork - Upon completion of the review the following are to be maintained with the data package and returned to the authorized person :

a. completed data assessment checklist and narrative (original)
b. Two copies of the data assessment narrative
c. **Communication** record Log (original and copy)

3.3 Rejection of Data - All values determined to be unacceptable on the Dioxin/Furan Analysis Data Sheet (Form I) must be flagged with an "R". The qualifier R means that due to significant QA/QC problems the analysis is invalid and it provides no information as to whether the compound is present or not. Once the data are flagged with R any further review or consideration is unnecessary. The qualifier "J" is used to indicate that due to QA/QC problems the results are considered to be estimated. The qualifier "NJ" indicates that there is presumptive evidence for the presence of the compound at an estimated value.

The data reviewer must explain in the data assessment narrative why the data was qualified. He or she must also indicate all items of contract non-compliance. When 2,3,7,8- substituted TCDD, TCDF, PeCDD and PeCDF data are rejected (flagged "R") or qualified "J" the project officer must be notified promptly. If holding times have not been exceeded reanalysis of the affected samples may be requested. All qualifications and corrections on the Analysis Data Sheet must be made in red pencil.

4.0 Definitions

CALIBRATION SOLUTION: solutions containing known amounts of selected analytes, internal standards and recovery standards that are analyzed prior to sample analysis. The solutions are used to determine the ratio of the instrument response of the analytes to that of the appropriate internal standard and the internal standards to that of the recovery standards.

CALIBRATION VERIFICATION (VER): a mixture of known amounts of analytes that is analyzed every 12 hours to demonstrate continued acceptable GC/MS performance and establish the retention time window for each homologue.

CDD: Chlorinated Dibenzo-p-Dioxin. The isomers and congeners of tetra- through octa-chlorodibenzo-p-dioxin.

CDF: Chlorinated Dibenzofuran. The isomers and congeners of tetra- through octa-chlorodibenzofurans.

CLEAN-UP STANDARD: only one labeled analyte (2,3,7,8-TCDD) is added to all samples extracts prior to any Clean-up procedure. This standard is used to differentiate between losses of analytes or internal standards during extraction and losses that occur during the various Clean-up procedures.

CONGENER: elements of the same group in the periodic table.

DEFLECTIONS: bend or broadening of a peak

ESTIMATED DETECTION LIMIT (EDL): the concentration of a analyte required to produce a signal with peak height of at least 2.5 times the background signal level. The EDL is calculated for each 2,3,7,8 substituted isomer for which the response of the quantitation and confirmation ions is less than 2.5 times the background level.

ESTIMATED MAXIMUM POSSIBLE CONCENTRATION (EMPC): the concentration of a given analyte that would produce a signal with a given area peak. The EMPC is calculated for each 2,3,7,8 substituted isomer for which the response of the quantitation and/or confirmation ions has signal to noise in excess of 2.5 times the background level but does not meet identification criteria.

Field Blank: An aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

FIELD CHAIN OF CUSTODY: see Traffic Report

GC: Gas chromatograph or gas chromatography.

GEL PERMEATION CHROMATOGRAPHY (GPC): removes many high molecular weight interferences that cause GC column performance to degrade. It may be used for all soil and sediment extracts and may be used for water extracts that are expected to contain high molecular weight organic compounds.

HOMOLOGUE: a member or members of a particular homologous series that has the same molecular weight but not necessarily the same structural arrangement. For example, the 28 pentachlorinated dibenzofurans are homologues.

HPLC: high performance liquid chromatography

HRGC/HRMS: high resolution gas chromatography/ high resolution mass spectrometry.

INITIAL CALIBRATION STANDARD SOLUTION (CS1-CS5): analysis of analytical standards for a series of different specified

concentrations. The initial calibration is used to define the linearity and dynamic range of the response of the mass spectrometer to the target compounds.

INITIAL PRECISION AND RECOVERY (IPR): must be performed by the laboratory to establish the ability to generate acceptable precision and accuracy **by analyzing four aliquots of the diluted PAR standard.** The standard deviation (s) of the concentration and the average concentration (x) for each unlabeled analyte must be within range established by the Method (Table 6). **An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.**

INTEGRATED ION CURRENT: electronic output to computer from instrument to provide a hard copy of area and height of a peak that may or may not be an analyte of interest.

INTERNAL STANDARDS (IS): labeled analytes are added to every sample and are present at the same concentration in every blank, quality control sample, and calibration solution. The IS are added to the sample before extraction and are used to measure the concentration of the analytes. In Method 1613B, the ISs are $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD.

ION ABUNDANCE RATIO: mathematical comparison of selected pair of ions stipulated by the method for each target analyte. The ratio between each pair of ions must fall within established limits. These ions are needed for the identification and quantitation of target analytes.

ISOMER: chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example 1,2,3,4-TCDD and 2,3,7,8-TCDD are structural isomers.

LABELED ANALYTE (or analog): an analyte that has isotopically carbon added to its chemical structure. These compounds are used to established identification (retention time) and used for quantitation of unlabeled analytes.

MASS/CHARGE: usually expressed as m/z.

METHOD BLANK (MB): an analytical control consisting of all reagents, internal standards and surrogate standards that is carried through the entire analytical procedure. The MB is used to define the level of laboratory background contamination.

Minimum Level (ML): The level at which the entire analytical system must give a recognizable signal and acceptable calibration point to the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and clean up procedures have been employed.

MAXIMUM CONCENTRATION LEVEL (MCL): Highest level of concentration for each analyte depending upon upper concentration of analyte. Usually used to determine upper level of the concentration range.

NON-CONGENER: elements not from the same group in the periodic table.

NON-2,3,7,8 SUBSTITUTED ANALYTES: analytes whose structure have positions other than 2,3,7,8.

ONGOING PRECISION AND RECOVERY (OPR): must be performed by the laboratory to establish the ability to maintain on a continuous basis, acceptable precision and accuracy. The standard deviation (s) of the concentration and the average concentration (x) for each unlabeled analyte must be within range established by the Method (Table 6).

PAR: Precision and Recovery standard. Secondary standard that is diluted and spiked to form IPR and OPR. The standard deviation (s) of the concentration and the average concentration (x) for each unlabeled analyte must be within range established by the Method (Table 6).

PERCENT MOISTURE: an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105°C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at this degree including water. %M is determined from decanted samples and from samples that are not decanted.

PERCENT VALLEY: see Resolution

PERFLUOROKEROSENE (PFK): compound used to establish mass spectral instrument performance for dioxin/furan analysis.

PERFORMANCE EVALUATION MIXTURE (PEM): See Performance Evaluation (PE) Sample.

PERFORMANCE EVALUATION (PE) SAMPLE: a chemical waste, soil or water sample containing known amounts of unlabeled CDDs/PCDFs used for Quality Assurance programs. There are 3 types of PE's available. PEM Blank which consists of uncontaminated soil and used to monitor possible crossover contamination of samples in the field and laboratory. PEM Interference Fortified Blank which is a soil containing matrix interference and spiked by the laboratory with target compounds. A PEM sample(s) is a soil sample containing known amounts of unlabeled TCDD or a mixture of TCDD and other PCDD/PCDF isomers. These PEMs are used to monitor the laboratory's performance.

PCDPE: Polychlorinated Diphenylether: isomers having the same SICP and ion ratios identical to furan isomers and are monitored for interference in furan qualitative and quantitative analysis.

Quality Control Check Sample (QCS): A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

RECOVERY: a determination of the accuracy of the analytical procedure made by comparing measured values from a fortified (spiked) sample against the known spiked values. Recovery is determined by the following equation:

$$\% \text{ Recovery} = \frac{\text{measured value}}{\text{known value}} \times 100\%$$

RELATIVE RETENTION TIME (RRT): ratio of the retention time of the analyte versus the retention time of the corresponding internal standard. RRT for each analyte must be within range established by the method.

RELATIVE RESPONSE (RR): the ratio of the area response of the mass spectrometer to a known amount of an analyte (unlabeled to labeled) versus a known concentration in standard solution, plotted using linear regression. The RR is used to determine instrument performance and is used in the quantitation calculations. RR are calculated using the following equation:

$$RR = \frac{(A_n^1 + A_n^2)\, C_l}{(A_l^1 + A_l^2)\, C_n}$$

$A_n^1 + A_n^2$ are the areas of the primary and secondary m/z's for the unlabeled compound.

$A_l^1 + A_l^2$ are the areas of the primary and secondary m/z's for the labeled compound.

C_l is the concentration of the labeled compound in the calibration standard.

C_n is the concentration of the unlabeled compound in the calibration standard.

Relative Standard Deviation (RSD): The standard deviation times 100 divided by the mean. Also termed "coefficient of variation".

RESPONSE FACTOR (RF): the ratio of the response of the mass spectrometer to a known amount of an analyte relative to that of a known amount of internal standard as measured in the initial and continuing calibrations. The RF is used to determine instrument

performance using correlation coefficient and is used in the quantitation calculations. RF are calculated using the following equation:

$$RF = \frac{(A_s^1 + A_s^2)\, C_{is}}{(A_{is}^1 + A_{is}^2)\, C_s}$$

$A_s^1 + A_s^2$ are the areas of the primary and secondary m/z's for the compound to be calibrated.

$A_{is}^1 + A_{is}^2$ are the areas of the primary and secondary m/z's for the internal standard.

C_s is the concentration of the compound in the calibration standard.

C_{is} is the concentration of the internal standard.

RESOLUTION: the separation between peaks on a chromatogram. Resolution is calculated by dividing the height of the valley between the peaks by the peak height of the smaller peak being resolved, multiplied by 100.

RINSATE: a portion of the solvent that is used to rinse sampling equipment. The rinsate is later analyzed to demonstrate that samples were not contaminated during collection.

SAMPLE DELIVERY GROUP (SDG): a unit within a single case that is used to identify a group of samples for delivery. A SDG is a group of 20 or fewer samples within a case, received over a period of time up to 14 calendar days. Data from all samples in a SDG are due concurrently. A SDG is defined by one of the following, whichever occurs first:

- Case: or
- each 20 samples within a case; or
- each 14 day calendar period during which samples in a case are received, beginning with receipt of the first sample in the case or SDG.

SELECTED ION MONITORING (SIM): a mass spectrometric technique whereby ions with predetermined mass/charge ratios (m/z) are monitored, as opposed to scanning MS procedures in which all m/z's between two limits are monitored.

SICP: A plot of ion abundance versus time for each ion which provides the retention time, peak area and height. This information is used for identification and quantitation of target analyte.

SIGNAL TO NOISE (S/N) RATIO: the ratio of analyte signal to random background signal. To determine the ratio, display each characteristic ion using a window 100 scans wide, and draw a base line from the lowest point in the 100 scan window. The noise is defined as the height of the largest signal (excluding signal due to CDDs/PCDFs or other chemicals) within the 100 scan window. The signal is defined as the height of the PCDD/PCDF peak. If the data system determines the ratio, the Contractor shall demonstrate comparability between the above criteria and the automated S/N determination. Chemical noise is left to the judgement of the analyst.

2,3,7,8 SUBSTITUTED ANALYTES: analytes whose structure has other positions as well as the 2,3,7,8 positions.

TOXICITY EQUIVALENCY FACTOR (TEF): a method of converting concentrations of CDDs/PCDFs to an equivalent concentration of 2,3,7,8-TCDD to obtain an estimation of the toxicity of the entire sample. The concentrations can be found on Form I PCDD-2 in the DFLM01.1 Statement of Work for Dioxin Analysis.

TRAFFIC REPORT (TR): (may also be called Field Chain of Custody), a sample identification form filled out by the sampler, which accompanies the sample during shipment to the laboratory and documents sample condition and receipt by the laboratory.

TWELVE HOUR TIME PERIOD: the 12 hour time period begins with the injection of the CS3 solution on the DB-5 (or equivalent)

column or the injection of the column performance solution on the SP-2331 (or equivalent) column. The 12 hour period continues until 12:00 hours have elapsed according to the system clock. To be included in a given 12-hour time period, a sample or standard must be injected with 12:00 hours of the CS3 solution or the column performance solution.

UNLABEL ANALYTE: target compound that has not been isotopically altered.

VALIDATED TIME OF SAMPLE RECEIPT (VTSR): the date on which a sample is received at the Contractor's facility. as recorded on the shipper's delivery receipt and sample traffic report.

WINDOW DEFINING MIXTURE (WDM): a mixture containing the first and last eluting isomer for each congener. The retention time for each first and last eluting isomer establishes the retention time window for each congener. All analytes in the standards (calibrations, internal standards, recovery standards, Clean-up standard) and identified analytes in samples must have a reported retention time within the established window. It is analyzed before any calibration standard, at the beginning of each 12 hour time period or when there is a shift greater than 10 seconds between retention time of recovery standards in standards or any analysis from retention time in recent calibration verification.

YES NO N/A

PACKAGE COMPLETENESS AND DELIVERABLES

CASE NUMBER:_____
LAB:_____
SITE:_____

1.0 Data Completeness and Deliverables

1.1 Does the Traffic Report or Field Chain of Custody list all samples? [ ] ___ ___

1.2 Is the Case Narrative present? [ ] ___ ___

1.3 Are the Case Number and SDG numbers contained in the case narrative? [ ] ___ ___

1.4 Do the Traffic Reports, Field Chain of Custody or Lab Case Narrative indicate problems with sample receipt, sample condition, analytical problems, or other comments affecting the quality of the data? ___ [ ] ___

ACTION: Use professional judgement to evaluate the effect of the noted problems on the quality of the data.

ACTION: As per region II requirements, if any sample analyzed as a soil, contains 50% to 90% water, all data shall be flagged as estimated "J". If a soil sample Contains more than 90% water, then qualify positive hits "J", and non detects "UJ".

ACTION: If sample cooler temperature was greater than 10 C, then flag all positive hits "J" And non detects "UJ".

2.0 Reporting Requirements and Deliverables

2.1 All deliverables must be clearly labeled with the Case number and the associated sample/traffic number. Missing or illegible or incorrectly labeled items must be identified. The Project Officer must immediately be contacted and requested to ask laboratory to submit the missing or incorrect items.

2.2 The following forms were taken from the CLP SOW. DFLM01.1 and should be specified in the Project Plan. Laboratories will not always use the exact CLP format for the forms. A comparison of CLP forms must be made against the Laboratory's version. Some information may not be found on the exact form as the CLP version but may be located on another form. As long as the information is present and accessible, it is not a problem. Are these forms (CLP or lab's version) present?

a. Sample Data Summary (Form I CDD-1) [ ] ___ ___

b. CDD/CDF Toxicity Equivalency Factor (Form I. CDD-2) [ ] ___ ___

c. Second Column Confirmation Summary (Form I, CDD-3) [ ] ___ ___

d. Total Homologue Concentration Summary (Form II CDD) [ ] ___ ___

e. CDD/CDF Spiked Sample Summary (Form III CDD-1) [ ] ___ ___

f. CDD/CDF Duplicate Sample Summary (Form III CDD-2) [ ] ___ ___

	YES	NO	N/A
g. CDD/CDF Method Blank Summary (Form IV-CDD)	[ ]	___	___
h. CDD/CDF Window Defining Mix Summary (Form V-CDD-1)	[ ]	___	___
I. Chromatographic Resolution Summary (Form V CDD-2)	[ ]	___	___
j. CDD/CDF Analytical Sequence Summary (Form V CDD-3)	[ ]	___	___
k. Initial Calibration (Form VI. CDD-1, CDD-2)	[ ]	___	___
l. Continuing Calibration (Form VII, CDD-1, Form VII, CDD-2)	[ ]	___	___

ACTION: If forms are missing, contact the Project Officer to confirm which forms if any were specified in the Project Plan. If the forms are required, inform the Project Officer or obtain written permission to contact the lab for explanation/resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the Data Assessment.

2.3 GC/MS Displays
Are the following GC/MS displays present?

a.	Standard and sample SIM chromatograms. SIM and TIC chromatograms must list date and time of analysis: the file name; sample number; and instrument I.D. number	[ ]	___	___
b.	Percent peak resolution valley	[ ]	___	___
c.	Window Defining Mixture raw data	[ ]	___	___
d.	SIM mass chromatograms must display quantitation ion, confirmation ion, and polychlorinated diphenylether ion, where applicable.	[ ]	___	___
e.	Integrated area and peak height must be listed for all peaks 2.5 times above background	[ ]	___	___

ACTION: If deliverables are missing, contact the Project Officer to request explanation/resubmittals or obtain written permission to contact the lab for explanation/resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the Data Assessment.

2.4 Are the following Chain of Custody Records and in-house Laboratory Control Documents present?

a.	Chain of Custody Records	[ ]	___	___
b.	Sample Shipment Records	[ ]	___	___
c.	Sample log-in sheets	[ ]	___	___
d.	GC/MS Standard and Sample Run Log in chronological order	[ ]	___	___
e.	Sample Extraction Log	[ ]	___	___

ACTION: If deliverables are missing, contact the Project Officer to request explanation/resubmittals

YES NO N/A

or obtain written permission to contact the lab for explanation/resubmittal. If the lab cannot provide missing deliverables, assess the effect on the validity of the data. Note in the Data Assessment.

2.5 Was the sample data package paginated and one sided? [___] ___ ___

ACTION: If no, document difficulties of reviewing data caused by lack of pagination in Data Assessment.

3.0 Holding Times

3.1 Have samples been analyzed within proper holding times?

a. For aqueous samples, 30 days from VTSR to extraction? [___] ___ ___

b. For soil/sediment samples, 30 days from VTSR to extraction? [___] ___ ___

c. For fish and tissue samples, one (1) year from VTSR to extraction? [___] ___ ___

d. For all samples 45 days from time of extraction to time of analysis? [___] ___ ___

ACTION: If holding times are exceeded, flag all positive hits as estimated ("J"), and non-detects as estimated "UJ". Holding time criteria do not apply to PE samples.
If holding times are grossly exceeded (e.g. by greater than two times the specified Technical holding times), either on the first analysis or upon reanalysis, flag positive hits as estimated "J", and flag non-detects as unusable "R".

Note: The data reviewer must note whether or not technical and contractual holding times were met.

4.0 Instrument Performance

4.1 Mass Calibration - Mass calibration of the MS must be performed prior to analyzing calibration solutions, blanks, samples, and QC samples. A static resolving power of at least 10,000 (10% valley definition) must be demonstrated at appropriate masses before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each 12 hour period of operation. Include in the narrative, minimum required resolving power of 10000 was obtained for perfluorokerosene (PFK) ion 380.9760. This is done by first measuring peak width at 5% of the maximum. This should not exceed 100 ppm. i.e., it should not exceed 0.038, for ion 380.9760. Resolving power, then is calculated using the formula,

Resolving Power = $m/\Delta m$ = 380.9760/0.038 = 10025.

NOTE: The mass calibration is generally not reported. Improper mass calibration may be detected by examining ion abundance ratios for initial and continuing calibration standards. If the mass calibration is not properly performed, the standards will not have ion abundance ratios within criteria.

4.2 Window Defining Solution/ Isomer Specificity Test Standards

The Window Defining Solution must contain the first and the last isomers of each homologue CDD/CDF, (the labeled and internal standards are optional). The solution also should contain a series of other TCDD analytes for the purpose of documenting the chromatographic resolution.

4.2.1 For analyses on a DB-5 (or equivalent) GC column, the chromatographic resolution is evaluated by the analysis of Isomer Specificity Test Standards at the beginning

YES NO N/A

of every 12 hour period. Was this performed accordingly? [___] ___ ___

ACTION: If the Isomer Specificity Test Standards was not analyzed at the required frequency, use professional judgement to determine the effect on the quality of the data. Document in Data Assessment under contract non-compliance.

4.2.2 Were all peaks labeled and identified on the Selected Ion Current Profiles (SICPs)? [___] ___ ___

4.2.3 Did the absolute retention time of the internal standards $^{13}C_{12}$-1,2,3,4-TCDD exceed 25.0 minutes on the DB-5 column and 15.0 minutes on the DB-225 column? (Method 1613B, Section 10.2.4) [___] ___ ___

4.2.4 Are the relative retention times of native and labeled CDD's and CDF's within the limits given in Table 2 of the method. (Method 1613B, Section 15.4.1.2) [___] ___ ___

ACTION: If no for sections 4.2.2, 4.2.3 and 4.2.4, assess the effect on the validity of the data. Note in the Data Assessment.

4.2.5 For DB-5 or equivalent, (Method 1613B, Section 15.4.2.2) the peak separation between the unlabeled 2,3,7,8-TCDD and the peaks representing any other TCDD analyte shall be resolved with a valley of ≤ 25 percent.
Was this criteria met? [___] ___ ___

% Valley = (x/y) x (100)

Y = The peak height of 2,3,7,8-TCDD analyte

X = The distance from the baseline to the bottom of the valley between the adjacent peaks.

ACTION: If the percent valley criteria are not met, qualify all positive data "J". Do not qualify non-detects.

4.2.6 Is the last eluting tetra chlorinated congener (1,2,8,9-TCDD) and the first eluting penta chlorinated congener (1,3,4,6,8-PeCDF) separated properly, since they elute within 15 seconds of each other? [___] ___ ___

ACTION: If one of the congener is missing, report that in the Data Assessment.

5.0 Initial 5-Point Calibration

The initial calibration standard solutions (CS1-CS5) must be analyzed prior to any sample analysis. However, initial calibration should be analyzed when the CS3 Calibration Verification (VER) or Isomer Specificity Test Standard do not meet performance criteria. The initial calibration standards must be analyzed on the same instrument using the same GC/MS conditions that were used to analyze the Window Defining Solution and the Isomer Specificity Test Standards.

Was the initial calibration performed at the frequency specified above? [___] ___ ___

5.1 The method allows the Laboratory to perform quantitative analysis by isotope dilution and internal standard, or to combine calibration solutions.

1. Isotope Dilution: performed for the fifteen 2,3,7,8-substituted CDDs and CDFs unlabeled analytes with labeled analytes added to the samples prior to extraction and for 1,2,3,7,8,9- HXCDD and OCDF (see sections 5.2.8 and 5.2.9). The relative response (RR) is calculated and the percent

YES NO N/A

coefficient of variation must be ≤ 20% over the 5 point range **(1613B sec. 10.5.4)** to use the average relative response for quantitation, otherwise a calibration curve must be used..

2. Calibration by Internal Standard: performed for non-2,3,7,8 substituted compounds having no labeled analytes in this method and for measurement of labeled compounds for intra laboratory statistics.. The response factor (RF) is calculated and the percent coefficient of variation must be ≤ 35% over the 5 point range **(1613B sec. 10.6.3)** to use the average response factor for quantitation, otherwise a calibration curve must be used.

3. Combined Calibration: performed by using solutions containing unlabeled, labeled compounds and internal standards. The requirements of each of the above methods are used. This method allows the laboratory to produce a single set of curves for isotope dilution and internal standard method.

5.1.1 The following MS/DS conditions must be used:

5.1.1.1 Mass calibration as per Section 4.1? [___] ___ ___

5.1.1.2 Were SIM data acquired for each of the ions listed in Table 8, including interfering ions? (see analytical method) [___] ___ ___

5.2 Were the following GC criteria met?

5.2.1 The chromatographic resolution between the 2,3,7,8-TCDD and the peaks representing any other unlabeled TCDD isomers must be resolved with a valley of ≤ 25 percent on the primary analysis (DB-5) column **(1613B** sec. **15.4.2.2)**. [___] ___ ___

5.2.2 The chromatographic resolution between the 2,3,7,8-TCDF and the peaks representing any other unlabeled TCDF isomers must be resolved with a valley of ≤ 25 percent on the confirmation (DB-225 or SP2330) analysis column. [___] ___ ___

5.2.3 For all calibration solutions, the relative retention time of peaks representing an unlabeled 2,3,7,8- substituted CDD or CDF must be within the limits given in table 2 of the Method. The retention times of the peaks representing non-2,3,7,8- substituted CDD or CDF's must fall within the retention time windows established by the Window Defining **Solution.** In addition, the absolute retention times of internal standards, $^{13}C_{12}$1,2,3,4-TCDD and $^{13}C_{12}$1,2,3,7,8,9-HxCDD shall not change by more than 15 seconds between the CS3 analysis and the analysis of any other standard. [___] ___ ___

5.2.4 Are the two SIM ions for each homolog must maximize simultaneously and within 2 seconds of the corresponding labeled analyte ions?**(1613B sec. 16.1)** [___] ___ ___

5.2.5 The relative ion abundance criteria for CDDs/CDFs listed in **Table 9** (see analytical method) must be met. [___] ___ ___

5.2.6 For all calibration solutions the signal to noise ratio (S/N) for the GC signal present in every SICP. including the ones for the labeled standards must be ≥ 10. [___] ___ ___

5.2.7 The percent relative standard deviations (% RSD) for the mean response factors (RRF) from the 17 unlabeled standards must be ≤ 20%, and those for the 15 labeled reference compounds must be ≤ 35%. [___] ___ ___

YES NO N/A

5.2.8 Labeled analyte 1,2,3,7,8,9-HxCDD is used as an internal standard in this method, and can not be used to quantitate corresponding unlabeled analyte. The unlabeled 1,2,3,7,8,9-HxCDD must be quantitated using the average of the responses of the labeled analytes of 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD. The concentration of the unlabeled 1,2,3,7,8,9-HxCDD is corrected for the average recovery of the other HxCDD's. Was the unlabeled 1,2,3,7,8,9-HxCDD quantitated correctly? [__] __ __

5.2.9 The labeled analog of OCDF is not added to the sample because of a potential interference. Unlabeled OCDF is quantitated against the labeled OCDD. The concentration of the unlabeled OCDF is corrected for the recovery of the labeled OCDD. Was the unlabeled OCDF correctly quantitated against the labeled OCDD. [__] __ __

ACTION:

1. If mass calibration criteria as specified in Section 4.1 was not met, note in Data Assessment.

2. If the selected monitoring ions specified in **Table 8** were not used for data acquisition, the lab must be contacted by the Project Officer for an explanation. If an incorrect ion was used, reject "R" all the associated data.

3. If the 25% percent valley for TCDD requirement was not met, quality positive data "J". Do not qualify non-detects. The tetra and penta (dioxins and furans) are affected. Heptas, Hexas and Octas are not affected.

4. If the ion abundance ratio for an analyte is outside the limits, flag the results for that analyte "R" (reject).

5. If the ion abundance ratio for an internal or labeled standard falls outside the QC limits flag the associated positive hits with "J". No effect on the non-detects.

6. If the signal to noise ratio (S/N) is below control limits, use professional judgement to determine quality of the data.

7. If the %RSD for each unlabeled analyte exceeds 20%, or the %RSD for each labeled analyte exceeds 35%, flag the associated sample positive results for that specific analyte as estimated ("J"). No effect on the non-detect data.

8. If 1,2,3,7,8,9-HxCDD was not calculated using the correct HxCDD response (average) factor, either manually recalculate the values for all standards and samples or contact Project Officer to request resubmittals from the laboratory.

9. If OCDF was not calculated using the correct response factor (OCDD), either manually recalculate the values for all standards and data or contact Project Officer to request resubmittals from the laboratory.

10. Non compliance of any other criteria specified above should be evaluated using professional judgement.

5.2.10 Spot check response factor calculations and ion ratios. Ensure that the correct quantitation ions for the unlabeled CDDs/CDFs and labeled standards were used. In addition, verify that the appropriate labeled standard was used for each analyte.

To recalculate the response factor, use the equation:

YES NO N/A

For target compounds (unlabeled analytes with corresponding labeled analytes):

$$RR = \frac{(A_{n1} + A_{n2}) \times Q_l}{(A_{l1} + A_{l2}) \times Q_n}$$

For labeled analytes. Internal standards and cleanup standard listed in Table 6 of method 1613:

$$RF = \frac{(A_{l1} + A_{l2}) \times Q_{is}}{(A_{is1} + A_{is2}) \times Q_l}$$

Note: There is only one m/z for $^{37}Cl_4$2.3.7.8-TCDD.

$A_{n1} + A_{n2}$ = integrated areas of the two quantitation ions of analytes of interest. (Target analyte, unlabeled compounds)

$A_{l1} + A_{l2}$ = integrated areas of the two quantitation ions of the appropriate labeled analytes compound.

$A_{is1} + A_{is2}$= integrated areas of the two quantitation ions of the appropriate internal standard.

Q_n = quantity of the unlabeled PCDD/PCDF analyte injected [pg]

Q_l = quantity of the appropriate labeled analytes compound [pg]

Q_{is} = quantity of the appropriate internal standard injected [pg]

ACTION: If calculations were not performed correctly, notify the Project Officer to initiate resubmittals from the laboratory.

6.0 System and Laboratory Performance (Calibration Verification and Isomer Specificity Test Standard)

At the beginning of a 12 hour shift during which analyses are performed, GC/MS system performance and calibration are verified for all unlabeled and labeled compounds. For these tests the calibration verification (VER) standard and the isomer specificity test standards shall be used to verify all performance criteria.

Only if the laboratory meets all performance criteria may samples, blanks, and precision and recovery standards be analyzed.

6.1 Calibration Verification

6.1.1 Was the relative ion abundance for CDDs/CDFs listed in **Table 9** of the analytical method met? (Method 1613B, Section 15.3.2) [___] ___ ___

6.1.2 Were the peaks representing each unlabeled and labeled compound in the verification standard present with signal to noise ratio (S/N) of $\geq$ 10? **(Method 1613B, Section 15.3.3)** [___] ___ ___

6.1.3 For each compound, was the concentration within the limit in Table 6 of the method? (Method 1613B, Section 15.3.5) [___] ___ ___

6.1.4 Were the absolute retention time of the internal standards $^{13}C_{12}$-1.2,3,4- TCDD and $^{13}C_{12}$1.2,3.7.8,9- HxCDD within $\pm$ 15 seconds of the retention times obtained during calibration? (Method 1613B, Section 15.4.1.1) [___] ___ ___

YES NO N/A

6.1.5 Were the relative retention times of the unlabeled and labeled CDDs and CDFs within the limits given by Table 2 of the method? (Method 1613B, Section 15.4.2.2) [ ] ___ ___

6.2 Isomer Specificity Test Standard

6.2.1 Was the chromatographic resolution between 2,3,7,8-TCDD and the peaks representing any other unlabeled TCDD isomers resolved with a valley of ≤ 25 percent on the primary analysis (DB-5) column? (Method 1613B, Section 15.4.2.2) [ ] ___ ___

6.2 Was the chromatographic resolution between 2,3,7,8- TCDF and the peaks representing any other unlabeled TCDF isomers resolved with a valley of ≤ 25 percent on the confirmation (DB-225 or SP2330) analysis. [ ] ___ ___

ACTION:

1. If the ion abundance ratio for an analyte is outside the limits, flag the results for that analyte "R" (reject).

2. If the signal noise ratio (S/N) is below control limits, use professional judgement to determine the quality of the data.

3. If an analyte concentration fell outside the acceptance criteria listed in Table 6 of the method.

   A. If the acceptance criteria for each unlabeled analyte and/or for each labeled analyte exceeds the range, flag the associated sample positive results for that specific analyte as estimated ("J"). No effect on the non-detect data.

   B. If the acceptance criteria for each unlabeled analyte and/or for each labeled analyte is below the range, flag the associated sample positive results as well as non-detects for that specific analyte as estimated ("J").

   C. If the acceptance criteria for each unlabeled analyte and/or for each labeled analyte is excessively below, ≤ 10% of the range, at the minimum, flag the associated sample positive results as well as non-detects for that specific analyte as estimated ("J"). However the validator may use professional judgement to accept or reject positive data and non-detects.

4. If the 25 percent valley for TCDD and TCDF requirement was not met, qualify positive data "J". Do not qualify non-detects. The tetras and pentas (dioxin and furans) are affected. Heptas, Hexas and Octas are not affected.

5. Non compliance of any other criteria specified above, in the method should be evaluated using professional judgement.

6.3 Spot check response factor calculations and ion ratios. Ensure that the correct quantitation ions for the unlabeled CDDs/CDFs and labeled standards were used. In addition, verify the appropriate labeled standard was used for each analyte.

7.0 Sample Data

NOTE: Any qualifications such as "J" applied to target compounds should be also applied to their associated total congeners concentration column.

7.1 Were the following MS/DS conditions used?

		YES	NO	N/A
7.1.1	SIM data were acquired for each of the ions listed in **Table 8** (see analytical method) including diphenylether interfering ions.	[ ]	___	___
7.2	Were the following identification criteria met?			
7.2.1	For the 2.3.7.8 substituted analytes found present and the corresponding labeled compound or internal standard in the sample extract. must show relative retention times at the peak height within the limits given in Table 2. (Method 1613B, Section 16.4)	[ ]	___	___
7.2.2	For non-2.3.7.8 substituted compounds (tetra through octa) found present. the retention time must be within the window established by the Window Defining **Solution**, for the corresponding homologue (Method 1613B. Section 16.4)	[ ]	___	___
7.2.3	All specified ions listed in **Table 8** for each isomer found present and the associated labeled compounds must be present in the SICP. The two SIM ions for the analyte. the labeled compound, and the internal standard must maximize simultaneously.(± 2 sec.) (Method 1613B, Section 16.1)	[ ]	___	___
7.2.4	The integrated ion current for each characteristic ion of the analyte identified as positive, must be at least 2.5 times background noise and must not have saturated the detector. (Method 1613B, Section 16.2)	[ ]	___	___
7.2.5	The integrated ion current for the labeled compounds, internal standards, and cleanup standard characteristic ions must be at least 10 times background noise. (Method 1613B, Section 16.2)	[ ]	___	___
7.2.6	The relative ion abundance criteria for all CDDs/CDFs found present must be within **the limits of Table 9, or ± 10% of the ratio in the midpoint CS3 calibration or calibration verification (VER) whichever is most recent.**	[ ]	___	___
7.2.7	The relative retention time of the unlabeled 2.3.7.8-substituted PCDD or PCDF must be within the limits given in Table 2 (Method 1613B, Section 16.4).	[ ]	___	___
7.2.8	The relative ion abundance criteria for the labeled compounds, cleanup. and internal standard must be met (Table 9 - Method 1613B).	[ ]	___	___
7.2.9	The analyte concentration must be within the calibration range. If not. dilution should have been made to bring the concentration within the calibration range. Was this criterion met?	[ ]	___	___

NOTE: The analytical method clearly states that samples containing analytes having concentrations higher than 10 times the upper MCLs should be analyzed using a less sensitive. high resolution GC/low resolution MS method.

7.2.10	The identification of a GC peak as a PCDF can only be made if no signal having a S/N ≥ 2.5 is detected at the same time in the corresponding polychlorinated diphenylether (PCDPE) channel. Was the above condition met?	[ ]	___	___

ACTION: 1. If the selected monitoring ions specified in Table 3 were not used for data acquisition, the lab must be contacted by the Project Officer for an explanation. If an incorrect ion was used, reject "R" all the associated data.

YES NO N/A

2. If the retention time of an analyte falls outside the retention time windows established by the associated Window Defining Mixture take the following action:

   A. If the analyte has a corresponding labeled analyte and is within 2 seconds of the labeled analyte, no action taken on positive data or non-detects.

   B. If the analyte has a corresponding labeled analyte and is outside 2 seconds of the labeled analyte, use professional judgement to determine qualifications for positive data or non-detects. At a minimum, "J" or "JN" positive data.

   C. If the analyte does not have a corresponding labeled analyte and is outside 2 seconds of the matching unlabeled analyte from the associated calibration, use professional judgement to determine qualifications for positive data or non-detects. At a minimum, "J" or "JN" positive data.

   D. If analyte meets identification criteria (7.2.2, 7.2.4, 7.2.5, 7.2.7) but does not meet ion abundance ratio criteria (7.2.8) and is not a labeled analog, the sample must be reanalyzed on a confirmation column. If confirmation analysis was not perform, reject "R" the failing analyte.

3. If the criteria listed in section 7.2.4 and 7.2.5 are not met but all other criteria are met, qualify all positive data of the specific analyte with "J".

4. If the analytes reported positive do not meet criteria for section 7.2.6, reject "R" all positive data for these analytes. Change the positive values to EMPC (Estimated Maximum Possible Concentration). Flag "J"

5. If the labeled compounds, internal standards and cleanup standards do not meet ion abundance criteria section 7.2.6. and 7.2.7. (Table 8 - analytical method) but they meet all other criteria, flag all corresponding data with "J".

6. If the lab reported values exceeding the calibration range flag those values with "J".

7. If peak deflections >50% are visible qualify particular compound with "J".

8. If PCDF was detected but an interfering PCDPE was also detected (see Section 7.2.9) and concentration not corrected for the interference, cross out the PCDF data. The reported value of PCDF is changed to EMPC.

9. If the lab did not monitor for PCDPEs, qualify all positive furan data "JN".

7.2.10 Spot check calculations for positive data and verify that the same labeled compounds used to calculate RFs were used to calculate concentration and EMPC. Ensure that the proper CDDs/CDFs and labeled compounds were used.

To recalculate the concentration of individual CDD/CDF analytes in the sample use the following equation:

All Matrices other than water

$$Cn\ (pg/g) = \frac{(A_{n1} + A_{n2}) \times Q_i}{W \times (A_{i1} + A_{i2}) \times RR}$$

Water

$$Cn\ (pg/L) = \frac{(A_{n1} + A_{n2}) \times Q_i}{}$$

YES NO N/A

$$V \times (A_{l1} + A_{l2}) \times RR$$

Where:

$A_{n1} + A_{n2}$ = integrated areas of the two quantitation ions of analyte of interest. (Target analyte)

$A_{l1} + A_{l2}$ = integrated areas of the two quantitation ions of the appropriate labeled analyte compound.

W = Weight (g) of sample extracted

V = Volume (L) of sample extracted

Q_l = Quantity (pg) of the appropriate labeled compound added to the sample prior to extraction.

RR = Calculated relative response from initial calibration. (see section 5.2.10)

ACTION: If the spot check calculations yielded positive hit concentrations with ≤ 15% Difference from those reported in Form I, correct manually. If the difference between the validator's value and the form 1's values are > 15% contact the Project Officer to request from the laboratory for an explanation and a copy of the laboratory's calculations.

7.3 Clean-up procedures

Clean-up may not be necessary for relatively clean samples (drinking waters, ground waters etc). If the matrix required clean-up, the laboratory has 4 different procedures to choose from. Before using any clean-up procedure, the laboratory must demonstrate that the Initial Precision and Recovery requirements of the method can be met using the clean-up procedure.

A labeled clean-up standard $^{37}Cl_4$2,3,7,8-TCDD is added to the sample just before the back extraction with base and acid procedure. This occurs before any recommended clean-up procedures are initiated.

7.3.1 Was the percent recovery of the clean-up standard within the recommended range listed **on Table 6 of the Analytical method?** [ ] ___ ___

ACTION: If no, and the recovery is less than 25%, qualify all data as estimated "J". If recovery is 0 %, qualify all positive data as estimated "J" and reject "R" all non-detects for that sample.

7.3.2 Check the chromatograms that clean-up procedure was needed for each sample. Were any clean-up procedures needed for either water or soil samples? ___ [ ] ___

ACTION: If yes, check extraction log to verify which clean-up procedures if any were performed. The laboratory is not limited to only one procedure.

1. If no clean-up was performed and the chromatograms indicated that some should have been performed. Use professional judgement to assess the effect on the interference on the validity of the data. Document lack of required clean-up for complex samples in Data Assessment.

2. If one type of clean-up was performed, but the chromatograms indicate that additional clean-up should have been utilized. Use professional judgement to assess the effect on the interference on the validity of the data. Document lack of additional clean-up for complex samples in Data Assessment.

7.3.3 If clean-up procedures were used, did the Laboratory perform clean-up procedures on the

YES NO N/A

Initial Precision and Recovery samples as required by the method? [__] __ __

ACTION: If no, Use professional judgement to assess the effect of the interference on the validity of the data. Document lack of IPR documentation for clean-up procedures in Data Assessment.

8.0 Estimated Detection Limits (EDL) *If required for the project*

8.1 Was an EDL calculated for each 2,3,7,8-substituted analyte that was not identified regardless of whether other non-2,3,7,8 substituted analytes were present? [__] __ __

ACTION: 1. If EDL or EMPC of an analyte which was not reported as a positive hit is missing, correct manually or contact the Project Officer to request from the laboratory corrections.

8.2 Use the equation below to check EDL calculations:

ALL MATRICES OTHER THAN WATER

$$EDL\ (pg/g) = \frac{2.5 \times Qis \times (Hx^1 + Hx^2) \times D}{W \times (His^1 + His^2) \times RR}$$

WATER

$$EDL\ (pg/L) = \frac{2.5 \times Qis \times (Hx^1 + Hx^2) \times D}{V \times (His^1 + His^2) \times RR}$$

Where:

Hx^1 and Hx^2 = peak heights of the noise for both quantitation ions of the 2,3,7,8-substituted isomer of interest.

His^1 and His^2 = peak heights of both the quantitation ions of the appropriate internal standards.

D = dilution factor

Qis, RR, W and V are previously defined.

NOTE: The validator should check the EDL data to verify that peak heights and not areas were used for this calculation. If the area algorithm was used, the validator should contact the Project Officer to request recalculations from the laboratory.

ACTION: If the spot check calculations yielded EDLs or EMPCs with $\leq$ 15% Difference from those reported in Form I, correct manually. If the difference between the validator's value and the Form I's values are > 15% contact the Project Officer to request from the laboratory for an explanation and a copy of the laboratory's calculations.

9.0 Estimated Maximum Possible Concentration (EMPC) *If required for the project*

9.1 Was an EMPC calculated for 2,3,7,8-substituted analytes that had S/N ratio for the quantitation and confirmation ions greater than 2.5, but did not meet all the identification criteria? [__] __ __

9.2 Use the equation below to check EMPC calculations:

YES NO N/A

All Matrices other than water

$$EMPC\ (pg/g) = \frac{(A_{n1} + A_{n2}) \times Q_1 \times D}{W \times (A_{l1} + A_{l2}) \times RR}$$

Water:

$$EMPC\ (pg/L) = \frac{(A_{n1} + A_{n2}) \times Q_1 \times D}{V \times (A_{l1} + A_{l2}) \times RR}$$

Action: 1. If EDL or EMPC of an analyte which was not reported as a positive hit is missing, correct manually or contact the Project Officer to request from the laboratory corrections.

2. If the spot check calculations yielded EDLs or EMPCs with ≤ 15% Difference from those reported in Form I, correct manually. If the difference between the validator's value and the Form I's values are > 15% contact the Project Officer to request from the laboratory for an explanation and a copy of the laboratory's calculations.

3. If EDLs or EMPCs for the most toxic analytes (TEF ≥ 0.05) are above reporting limits, contact the project office to recommend sample reanalysis.

10.0 Method Blanks

10.1 Has a method blank per matrix been extracted and analyzed with each batch of 20 samples? [___] ___ ___

10.2 If samples of some matrix were analyzed in different events (i.e. different shifts or days) has one blank for each matrix been extracted and analyzed for each event? [___] ___ ___

10.3 Acceptable method blanks must not contain any signal of 2,3,7,8-TCDD, or 2,3,7,8-TCDF, equivalent to a minimum levels listed in Table 2 **or above one third the regulatory compliance level.**. Was this criteria met? (Method 1613B, Section 9.5.2) [___] ___ ___

10.4 For other 2,3,7,8- substituted CDD/CDF isomers of each homologue, the allowable concentration in the method blank is less than minimum level listed in Table 2 (< 5 ng/Kg for soils and 50 pg/L for waters). Was this criteria met? [___] ___ ___

ACTION: 1. If the proper number of method blanks were not analyzed, document in Data Assessment. If the validator feels that the validity of the data is seriously compromised and validation of data without the method blanks would be flawed then notify the Project Officer. If decision is made to proceed with the validation process, consider the following actions: no action taken on non-detected analytes. If an analyte has a reported concentration that is > 5 times the EDL, qualify "J" and all concentrations ≤ 5 times the EDL are qualified "R" due to possibility of contamination.

2. If the method blank is contaminated with 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD, 1,2,3,7,8-PeCDF or 2,3,4,7,8-PeCDF at a concentration higher than the minimum levels in Table 2, reject all contaminant compound positive data for the associated samples "R" and notify the Project Officer to initiate reanalysis.

3. A. If the method blank is contaminated with any of the analytes mentioned in Action # 2 at a concentration of less than the minimum levels in Table 2 specified in the method or of any other 2,3,7,8-substituted analytes at any concentration and the concentration in the sample is less than five times the concentration in the blank, transfer the sample results to the EMPC/EDL column and cross-out the value in

YES NO N/A

the concentration column in order to present the data as a non-detect.

B. If the concentration in the sample is higher than five times the contamination concentration in the blank, no action is needed.

11.0 Labeled Compound Recoveries

11.1 Were the samples spiked with all the labeled compounds as specified in the method? [ ] ___ ___

11.2 Have labeled compounds' recoveries been within the required limits? [ ] ___ ___

11.3 If not, were samples reanalyzed? [ ] ___ ___

ACTION: 1. If the labeled compound recovery was below 25 percent, reject "R" all associated non-detect data (EMPC/EDL) and flag with "J" the positive data for the associated compound.

2. If the labeled compound recovery is above the upper limit (150 percent) flag associated positive data with "J". No effect on non-detects.

3. If the labeled compound recovery is less than 10%, qualify positive hits and non-detects associated with the failed labeled compound "R" (Reject). When highly toxic analytes (TEF$\geq$ 0.05) are affected, notify Project Officer to initiate reanalysis.

Recalculate the percent recovery for each labeled standard in the sample extract, Rec_l, using the formula:

$$\% Rec_l = \frac{(A_{l1} + A_{l2}) \times Q_{is} \times 100}{(A_{is1} + A_{is2}) \times RF \times Q_l}$$

$A_{l1} + A_{l2}$ = integrated areas of the two quantitation ions of the appropriate labeled compound.

$A_{is1} + A_{is2}$= integrated areas of the two quantitation ions of the appropriate internal standard.

Q_l = quantity of the appropriate labeled compound

Q_{is} = quantity of the appropriate internal standard injected

RF was defined, previously.

12.0 Internal Standard Area Response

There is no method criterion for the Internal Standard area response. However, because it is very critical in determining instrument sensitivity, the Internal Standard area response should be checked for every sample. The two standards $^{13}C_{12}$1,2,3,4-TCDD and $^{13}C_{12}$1,2,3,7,8,9-HxCDD are referred to as Internal Standards in this method. In other Dioxin methods, the two standards are called Recovery Standards.

12.1 Are the internal standard areas for every sample and blank within the upper and lower limits of each associated initial calibration CS3?

Area upper limit= +100% of internal standard area.
Area lower limit= -50% of internal standard area. [ ] ___ ___

12.2 Is the retention time of each internal standard within 15 seconds of the associated initial calibration CS3 standard? [ ] ___ ___

YES NO N/A

ACTION: 1. If the internal standard area is outside the upper or lower limits, flag all related positive and non-detect data (EMPC/EDL) with "J" regardless whether the lab's labeled compound recoveries met specifications or not.

2. If extremely low area counts (<25%) are reported, flag all associated non-detect data as unusable "R" and the positive data "J".

3. If the retention time of the internal standards differs by more than 15 seconds from the initial calibration CS3, use professional judgement to determine the effect on the results. A time shift of more than 15 seconds may cause certain analytes to elute outside the retention time window established by the GC window defining/column performance check solution. A constant shift could be also the result of a leak.

NOTE: Action 1 and 2 are recommendations only since this criterion is not a method requirement. These guidelines are based on other methods, previously validated data packages and Region II recommendations. If method blanks have low area responses as well as the samples, the validator should seriously consider qualifying the data for this criterion. Action 3 is a method requirement.

13.0 Second Column Confirmation

13.1 Any sample in which 2,3,7,8-TCDF is identified on a DB-5 column, must have a confirmation analysis (Method 1613B, section 16.5). Was a second column confirmation performed? [___] ___ ___

13.2 Was the sample extract reanalyzed on a 30 m DB-225, fused silica capillary column, for 2,3,7,8-TCDF using the GC/MS conditions given in Section 10.1.1 of the analytical method? [___] ___ ___

NOTE: The concentration of 2,3,7,8-TCDF obtained from the primary column (DB-5) should only be used for qualification, due to better QC data associated with the primary column. Also note that the confirmation and quantitation of 2,3,7,8-TCDF may be accomplished on a SP-2330 GC column.

ACTION: If confirmation is missing, use professional judgement, or contact the Project Officer for assistance.

13.3 Did the second column meet the calibration and linearity specification in Sections 5.0 and 6.0 above? [___] ___ ___

ACTION: If no, refer to section 5.0 and 6.0 for appropriate action.

13.4 Was the % D of the quantitation results of the two columns less than 50? [___] ___ ___

ACTION: Note in data assessment the differences, use professional judgement to decide which column data to report for TCDF. No other action is needed since this is not a method requirement but a technical recommendation.

14.0 Sample Reanalysis

14.1 The Project Officer will evaluate the need for reanalyzing the samples with qualified data based on site-specific Data Quality Objectives.

14.2 Due to a variety of situations (see below) that may occur during sample analysis, the laboratory is required to reanalyze or re-extract and reanalyze certain samples. If a reanalysis was required but was not performed, contact the Project Officer to initiate reanalysis. List in data assessment all re-extractions and reanalyses

YES NO N/A

and identify the CDD/CDF sample data summaries which must be used by the data user (when more than one analysis is submitted for a sample).

Lab must re-extract and/or re-analyzed samples when the following criteria are not met:

1. Contaminated method blank at concentrations above the minimum levels (Table 2)

2. Labeled compound recoveries outside acceptable ranges listed on Table 6 of Analytical method.

3. Exceedance of calibration range by an analyte (dilution or re-extract using a smaller aliquot).

4. Recovery of labeled compounds outside acceptable limits listed on Table 6 of the Analytical method in a diluted sample (re-extracted using a smaller aliquot).

ACTION: For criteria 1, 2, or 3, notify the Project Officer to discuss possible re-analysis of sample by the laboratory.

For criteria 4, If the calibration was verified and the re-extracted sample still does not meet labeled recovery requirements, then the method does not apply to the sample. The results are not reportable for regulatory purposes (Method 1613B, section 18.4.4). Notify the Project Officer of problem to initiate re-analysis of sample using a different method. Document in Data Assessment.

15.0 Precision and Recovery (PAR)

The laboratory is required to show initial demonstration of capability, to evaluate and document data quality. Laboratory performance is compared to established performance criteria to determine if results of analyses meet the performance characteristics of the method.

The laboratory must perform and submit data to establish the ability to generate acceptable precision and accuracy.

15.1 Did the laboratory analyzed an Initial Precision and Recovery (IPR) standard as outlined in section 9.2 required by the analytical method? [ ] ___ ___

ACTION: If no, contact the Project Officer to request resubmittals from the laboratory.

If data is not available, discuss with the Project Officer the feasibility of continuing with validation. If a decision is made to proceed with validation, use professional judgement. All data at a minimum should be qualified as estimated "J". Technically according to the method, data and system performance is unacceptable for all compounds. Analyses should not have continued as per the method. Document under contract non-compliance in Data Assessment.

15.2 Did the IPR standard deviation (s) and average concentration (x) passed criteria as outlined in Table 6 of the method? [ ] ___ ___

ACTION: If no, refer to action from section 15.1.

The laboratory must analyzed an Ongoing Precision and Recovery standard (OPR) periodically, at the beginning of 12 hour shift after the analysis of the CS3 calibration verification (VER), and before the analysis of any sample in each set .

15.3 Was the Ongoing Precision and Recovery (OPR) standard analyzed at the required frequency? [ ] ___ ___

15.4 Did the OPR standard passed the concentration criteria limits in Table 6 of the method? [ ] ___ ___

YES NO N/A

ACTION: If no, refer to action from section 15.1. All samples that do not have a passing OPR standard are potentially affected for that analyte.

The following sections may be incorporated in the validation process on a case by case basis depending upon the requirements of the Project Plan. Sometimes a laboratory will provide data for some of the following sections on a routine basis. If not a requirement of the Project Plan, then professional judgement is needed to qualify data based on additional information.

16.0 Isomer Specificity and Toxicity Equivalency Factor (TEF)

NOTE: The TEF value concentrations can be found in the DFLM01.1 Statement of Work for Dioxin Analysis Form I PCDD-2.

When calculating the 2,3,7,8-TCDD Toxicity Equivalency of a sample only those 2.3,7,8 substituted isomers that were positively identified in the sample must be included in the calculations. The sum of the TEF adjusted concentration is used to determine when a second column confirmation is required to achieve analyte specificity.

16.1 Did the lab include EMPC or EDL values in the toxicity equivalency calculations? [___] ___ ___

16.2 Were all samples, whose toxicity equivalency exceeded the required values were reanalyzed on a confirmation column to establish analyte specificity? [___] ___ ___

ACTION: 1. If yes, the toxicity equivalency calculations were not calculated properly, notify the Project Officer to arrange for laboratory resubmittals.

2. If the toxicity equivalency exceeded the required limits (0.7 µg/Kg for soil/ sediment, 7 ng/L for aqueous and 7 µg/Kg for chemical waste samples), and the lab failed to reanalyze the samples on a specific secondary column, notify Project Officer. Reanalysis may be initiated.

NOTE: Any qualifications such as "J" applied to target compounds should be also applied to their associated total congeners concentration.

17.0 Rinsate Blank *(Region 2 QA guidelines recommend rinse blanks for all projects)*

17.1 One rinsate blank should be collected for each batch of 20 soil samples or one per day whichever is more frequent. Were rinsate blanks collected at the above frequency? [___] ___ ___

17.2 Do any rinsate blanks show the presence of 2,3.7,8-TCDD, 2.3.7.8-TCDF, and 1.2.3.7,8-PeCDD at amounts > .5 µg/L or any other analyte at levels > 1 µg/L? [___] ___ ___

ACTION: If any rinsate blank was found to be contaminated with any of the CDDs/CDFs notify the Project Officer to discuss what proper action must be taken.

If any qualification is needed due to rinsate blank contamination, follow the guidelines outlined under Method Blanks, section 10, Actions 2 and 3.

18.0 Field Blanks

18.1 The field blanks are PEM samples (blind blanks) supplied to Laboratory at the frequency of one field blank per 20 samples or one per samples collected over a period of one week, which ever comes first. A typical "field blank" will consist of uncontaminated soil. The field blanks are used to monitor possible cross contamination of samples in the field and in the laboratory.

Were the following conditions met?

YES NO N/A

18.2 Acceptable field blanks must not contain any signal of 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD and 1,2,3,7,8-PeCDF equivalent to a concentration of > 20 ng/Kg. [___] ___ ___

18.3 For other 2,3,7,8 substituted CDD/CDF analytes of each homologue the allowable concentration in the field blank is less than the upper MCLs listed in the method. [___] ___ ___

ACTION: When the field blank is found to be contaminated with target compounds, apply the same action as described for the Method Blank, section 10, Actions 2 and 3.

NOTE: Ask Project Officer to verify that the PEM blank (field blank) did not contain any CDD/CDF analytes and ask their assistance in the evaluation of the PEM field blank.

19.0 PEM Interference Fortified Blanks

NOTE: This type of blank may not be available at this time. In many cases, laboratories will substitute matrix spike/matrix spike duplicate (MS/MSD). If a PEM Interference Fortified blank(s) were not analyzed but MS/MSD data were submitted, skip this section and go onto to section 21.

19.1 One known blank usually an interference fortified soil/sediment sample is supplied to the Laboratory. The frequency of this QC sample is one per group of 20 environmental samples or one per samples collected over one week period, whichever occurs first. The sample is spiked by the laboratory with the appropriate volume of the matrix spiking solution and then extracted and analyzed with other samples.

19.2 Was a fortified PEM blank analyzed at the frequency described above? [___] ___ ___

19.3 Was the percent recovery of 2,3,7,8-TCDD and other 2,3,7,8-substituted compounds within the 50 to 150 percent control limits? [___] ___ ___

ACTION: 1. If the recovery of a 2,3,7,8-substituted analytes falls outside the 50-150 percent control limit, flag all positive and non-detect data of the same and related analytes in the same homolog series with "J". However, if the recovery is below 20%, qualify all associated non-detects "R" and positive hits as "J". Notify the Project Officer. Reanalysis may be initiated.

2. If no fortified PEM blank was analyzed, use professional judgement to assess data validity.

20.0 Matrix Spike (MS) Field Sample

Note: Matrix spike is not required by this method although Labs may routinely perform this analysis as part of internal QA/QC and submit this data as part of the package. Verify requirements with Project Officer.

20.1 Was a matrix spike analyzed at the frequency of one per SDG samples per matrix? [___] ___ ___

20.2 Was the percent recovery of 2,3,7,8-TCDD and other 2,3,7,8-substituted CDDs/CDFs within 60 to 140 percent? [___] ___ ___

ACTION: If problems such as interferences are observed, use professional judgement to assess the quality of the data. The 60-140% limits of the matrix spike data may be used to flag data of the spiked sample only. The matrix spike data of the PE blank sample are more important and must be used primarily in data validation.

20.3 Was a matrix spike duplicate analyzed as per section 11.1 and 11.2? [___] ___ ___

YES NO N/A

ACTION: No action required. A matrix spike duplicate is not required. Use professional judgement if there is a large difference in concentrations reported between MS and MSD. Qualifications if any, can only be performed on the sample that was used for this criteria.

21.0 Environmental Duplicate Samples *(recommended in Region 2 for all Projects)*

NOTE: Do not confuse an environmental duplicate with a matrix spike duplicate. An environmental duplicate is a sample that has been divided into 2 parts (extracted and analyzed as two different samples) or as 2 separate samples from the same location sent by the sampling crew. This sample is not spike with any additional compounds other than those compounds required by the method for analysis of all routine samples.

21.1 For every batch of 20 samples or samples collected over a period of one week, whichever is less, there must be a sample designated as duplicate. Were duplicate samples collected at the above frequency? [___] ___ ___

21.2 Did results of the duplicate samples agree within 25% relative difference for 2,3,7,8-substituted analytes and 50% for the rest of the analytes? [___] ___ ___

ACTION: The duplicate results can be used in conjunction of other QC data. Use professional judgement.

22.0 REFERENCES

The following references are cited in Method 1613. They are important references for technical information and are submitted here as part of this method's documentation.

1. "Analytical Procedures and Quality Assurance Plan for the Determination of PCDD/PCDF in Fish", USEPA Environmental Research Laboratory, 6201 Congdon Boulevard, Duluth, NH 55804, April 1988.

2. Barnes, Donald G., Kutz, Frederick W., and Bottimore, David P., "Update of Toxicity Equivalency Factors (TEFs) for Estimating Risks Associated with Exposure to Mixtures of Chlorinated Dibenzo-p-dioxins and dibenzofurans (CDDs/CDFs)", Risk Assessment Forum, USEPA, Washington, DC 20460, February 1989.

3. Lamparski, L.L., and Nestrick, T.J., "Determination of Tetra-, Hexa-, Hepta-, and Octachlorodibenzo-p-dioxin Isomers in Particulate Samples at Parts per Trillion Levels", Analytical Chemistry, 52: 2045-2054, 1980.

4. "Measurment of 2,3,7,8-Tetrachlorinated Dibenzo-p-dioxin (TCDD) and 2,3,7,8-Tetrachlorinated Dibenzofurans (TCDF) in Pulp, Sludges, Process Samples and Waste-waters from Pulp and Paper Mills", Wright State University, Dayton, OH 45435, June 1988.

5. Method 1613-Revision B- Tetra through Octa- chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, USEPA, Washington, DC, 20460, October 1994

6. "Method 613--2,3,7,8-tetrachlorodibenzo-p-dioxin", 40 CFR 136 (49 FR 43234), October 26, 1984, Section 4.1.

7. "NCASI Procedures for the Preparation and Isomer Specific Analysis of Pulp and Paper Industry Samples for 2,3,7,8 TCDD and 2,3,7,8 TCDF", National Council of the Paper Industry for Air and Stream Improvement, 260 Madison Avenue, New York, NY 10016. Technical Bulletin No.551, Pre-release Copy, July 1988.

8. Provost, L.P., and Elder, R.S., "Interpretation of Percent Recovery Data", American Laboratory, 15: 56-83, 1983

YES NO N/A

9. Stanley, John S., and Sack, Thomas M., "Protocol for the Analysis of 2,3,7,8-Tetrachlorodibenzo-p-dioxin by High Resolution Gas Chromatography/High Resolution Mass Spectrometry", USEPA EMSL, Las Vegas, Nevada 89114. EPA 600/4-86-004. January 1986.

10. Tondeur, Yves, "Method 8290: Analytical Procedures and Quality Assurance for Multimedia Analysis of Polychlorinated Dibenzo-p-dioixin and Dibenzofurans hy High Resolution Gas Chromatography/High Resolution Mass Spectrometry", USEPA ENSL, Las Vegas, Nevada. June 1987.

11. Tondeur. Yves, "Proposed GC/MS Methodology for the Analysis of CDDs and CDFs in Special Analytical Services Samples", Triangle Laboratories. Inc., 801-10 Capitola Dr., Research Triangle Park, NC 27713, January 1988; updated by personal communication September 1988.

ATTACHMENT A

CDFs/CDD DATA ASSESSMENT

SDG No.
LABORATORY:
SITE:

DATA ASSESSMENT

The current Functional Guidelines for evaluating dioxin/furans organic data have been applied.

All data are valid and acceptable except those analytes which have been qualified with a "J" (estimated), "N" (presumptive evidence for the presence of the material), "U"(non-detects), "R" (unusable), or "JN"(presumptive evidence for the presence of the material at an estimated value). All action is detailed on the attached sheets.

Two facts should be noted by all data users. First, the "R" flag means that the associated value is unusable. In other words, due to significant QC problems, the analysis is invalid and provides no information as to whether the compound is present or not. "R" values should not appear on data tables because they can not be relied upon, even as a last resort. The second fact to keep in mind is that no compound concentration, even if it has passed all QC tests, is guaranteed to be accurate. Strict QC serves to increase confidence in data but any value potentially contains error.

Reviewer's
Signature:_____ Date:__/__/200_

Verified By:_____ Date:__/__/200_

GENERAL COMMENTS:

HOLDING TIME:

BLANK CONTAMINATION:

WINDOW DEFINING MIXTURE:

ION ABUNDANCE:

CALIBRATIONS:

RESOLUTION:

LABELED STANDARDS PERFORMANCE:

INTERNAL STANDARDS:

PEAK IDENTIFICATION:

MATRIX SPIKE/ ENVIRONMENTAL DUPLICATE:

CONFIRMATIONS:

OTHER QC OUT OF SPECIFICATION:

SYSTEM PERFORMANCE AND OVERALL ASSESSMENT:

CONTRACT PROBLEMS NON-COMPLIANCE:

RE-EXTRACTION, REANALYSIS OR DILUTIONS:

DO NOT USE USE

FIELD DOCUMENTS:

Validation SOP
No. V-3

EDS SOP RAD-1 Rev. 4, 7/07

DATA VALIDATION SOP

RAD-1, REV. 4

RADIOCHEMICAL ANALYSES

ENVIRONMENTAL DATA SERVICES

RADIOCHEMICAL ANALYSES VALIDATION CHECKLIST (SOP)

SITE:

DATE:

SDG:

	Y	N	N/A
Data Completeness and Deliverables			
Have any missing deliverables been received and added to the data package?	_____	_____	_____
ACTION: Call lab for explanation/resubmittal of any missing deliverables. If the lab cannot provide them, note the effect on review of the data in the non-compliance section of the data assessment narrative.			
Validation Radiochemical Data			
The data validation criteria outlined in this section applies to radiochemical data obtained via beta and gamma spectrometry.			
RADIOCHEMICAL ANALYSES			
Sample Receipt/Lab Case Narrative			
Are all chains-of-custody present for all samples?	_____	_____	_____
ACTION: If no, prepare Telephone Record Log and contact lab for submission of missing or illegible copies.			
Do chain of custody records or lab case narrative indicate any problems with sample receipt , condition of samples, analytical problems or special circumstances affecting the quality of the data?	_____	_____	_____

Y N N/A

Holding Times

Have any radiological technical holding times, determined from date of collection to date of analysis, been exceeded? _____ _____ _____

The holding time for soil is 6 months from date samples were collected, with the exception of Be-7 (45 days).

Table of Holding Time Violations

Sample ID	Sample Matrix	Preserved?	Date Sampled	Date Lab Received	Date Analyzed

ACTION: If technical holding times are exceeded document in the Data Assessment Narrative that holding times were exceeded. If analyses were done more than 14 days beyond holding time, either on the first analysis or upon re-analysis, the reviewer must use professional judgment to determine the reliability of the data and the effects of additional storage time on the data.

Sample Replicate Analysis

Is a duplicate summary form present? _____ _____ _____

Were replicates analyzed at the required frequency? _____ _____ _____

One per twenty field samples analyzed by each system? _____ _____ _____

ACTION: If no, prepare Telephone Record Log and contact laboratory for explanation/resubmittals. Note any impact on data quality in the Data Assessment Narrative.

Raw data present should include the following:

A. Detector used
B. Analyst initials
C. Date analyzed
D. Sample I.D.
E. Value obtained for initial analyses
F. Value obtained for replicate analyses
G. Mean value
H. Duration of counts in minutes
   - samples
   - background
I. CPM's for samples and background

	Y	N	N/A
Are all associated replicate values within allowable limits (overlap of the 2 sigma error bands or mean difference value between results reported of less than 3)?	_____	_____	_____

$$\text{mean difference} = \frac{|\text{Sample activity} - \text{duplicate activity}|}{\sqrt{(\text{sample error 2-sigma})^2 + (\text{duplicate error 2-sigma})^2}}$$

ACTION: Qualify associated data as estimated if the above criterion is not met.

Blanks

Is a method blank summary present?	_____	_____	_____
Frequency of Analysis:			
Has a reagent/method blank been analyzed for Pb-210 with each analytical batch?	_____	_____	_____
Has a blank container been counted by gamma detector each week associated samples are counted?	_____	_____	_____

ACTION: If any method blank data are missing, prepare a Telephone Record Log and contact lab for an explanation/ resubmittal. If method blank data are not available, reject all associated positive data. However using professional judgment, the data reviewer may substitute field blank or trip blank data for missing method blank.

Contamination

Do any of the method/instrument/reagent blanks have positive results for radiological isotopes of concern?	_____	_____	_____

When applied as described below, the contaminant concentration in these blanks are multiplied by any dilution factor and corrected for % moisture.

ACTION: Prepare a list of samples associated with contaminated blanks.

Y N N/A

ACTION: If a compound is found in a blank, but not found in the sample, no action is taken.

If a blank has a positive result for an analyte and associated samples are positive for the analyte, qualify associated sample data as follows:

Calculate the mean difference between each associated positive sample result and the positive method blank value. Those sample results exhibiting a mean difference value of 3 or less when compared to the method blank result are considered to not be statistically different than the method blank and therefore are qualified "U" due to method blank contamination. Those sample results exhibiting a mean difference value of greater than 3 when compared to the blank value are considered to be statistically different and therefore no qualification of these results is necessary.

The reviewer should note that the blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. These factors must be taken into consideration when applying the Criteria described above, such that a comparison of the total contamination is actually made.

Target Analytes

Are the radiochemical analysis data summaries present (example: Form I RAD) with required header information, for each of the following:

a. Samples and or fractions as appropriate? _____ _____ _____

b. Duplicates? _____ _____ _____

c. Blanks? _____ _____ _____

Are the radiological raw data including beta and gamma instrument printouts and calculations in the sample package for each of the following:

a. Samples and/or fractions as appropriate? _____ _____ _____

b. Duplicates? _____ _____ _____

c. Blanks? _____ _____ _____

ACTION: If any data are missing prepare Telephone Record and contact lab to obtain explanation/resubmittals. Note any impact on the data quality in the Data Assessment Narrative.

	Y	N	N/A
Analyte Quantitation and Minimum Detectable Concentration (MDC) Values			
Are there any transcription/calculation errors in data summary results?	_____	_____	_____
Check at least two positive values. Were any errors found?	_____	_____	_____
Are the minimum detectable concentration values adjusted to reflect sample dilutions?	_____	_____	_____

ACTION: If errors are large, contact lab for explanation/resubmittal, make any necessary corrections and note errors in the Data Assessment Narrative.

Have all results been reported with associated counting error at 2-sigma, Critical value and MDC?	_____	_____	_____
Have all results been flagged appropriately?	_____	_____	_____

Results reflecting activity less than the associated critical value are flagged "U" because they are not statistically positive. Results that are greater than the critical value but less than the MDC are flagged "G".

ACTION: If data was not properly reported, contact laboratory for explanation/correction and re-submission of electronic and hard copy data.

Do all Cs-137 results at 0.1 pci/g activity have associated counting uncertainties at 2-sigma that are 0.03 pci/g or less?	_____	_____	_____

ACTION: If yes, provide a list of affected samples in the data assessment narrative.

BETA Spectrometry Initial Calibration			
Are the initial calibration summary forms present and complete for each detector used to quantitate samples?	_____	_____	_____

	Y	N	N/A
Are the following records present for each detector used:			
Identification of Detector?	_____	_____	_____
Analyst's initials?	_____	_____	_____
Date and time of calibration?	_____	_____	_____
Name/Activity/Date of certified NBS material?	_____	_____	_____
Counts per minute?	_____	_____	_____
Duration of counting?	_____	_____	_____
Calculated Efficiencies?	_____	_____	_____

ACTION: Contact the laboratory for submission of any missing data .

Are efficiencies of each detector used greater than 15%?	_____	_____	_____

ACTION: Qualify as estimated results associated with a non-compliant calibration.

BETA Spectrometry Continuing Calibration

Are the continuing calibration summaries present and complete?	_____	_____	_____
Has a continuing calibration standard been analyzed twice every week of sample analysis per instrument?	_____	_____	_____

ACTION: List below all sample analysis that were not within one week of the previous continuing calibration set.

_____

_____

_____

ACTION: If any forms are missing or if a continuing calibration standard was not analyzed twice during each week of every sample analysis, prepare Telephone Log and contact lab for explanation/resubmittal.

	Y	N	N/A
Are the following continuing calibration records present for each detector used:			
Control charts and logs defining check source results.	_____	_____	_____
ACTION: Contact laboratory for submission of any missing data.			
Are the check source count rates within three standard deviations of the mean?	_____	_____	_____
ACTION: Qualify as estimated results associated with a non-compliant calibration.			

Recovery Factors

For the Lead-210 analyses is the chemical recovery or yield greater than 20%?	_____	_____	_____
ACTION: Reject all associated data if recovery is less than 20%.			

GAMMA Spectrometry Continuing Calibration

Are the continuing calibration summaries present and complete?	_____	_____	_____
Has a continuing calibration standard been analyzed twice during each week of sample analysis per instrument?	_____	_____	_____

ACTION: List below all sample analysis that were not within one week of the previous continuing calibration set.

_____

_____

_____

ACTION: If any forms are missing or if a continuing calibration standard was not analyzed twice during each week of every sample analysis, prepare Telephone Log and contact lab for explanation/resubmittal.

	Y	N	N/A
Are the following continuing calibration records present for each detector used:			
Control charts and logs defining check source results and efficiency limits?	_____	_____	_____
Blank results for background control (gamma only)?	_____	_____	_____

ACTION: Contact laboratory for submission of any missing data.

Are efficiencies of selected energies within three standard deviations of the mean?	_____	_____	_____
Are the resolutions of each peak less than 5 KEV?	_____	_____	_____

ACTION: Qualify as estimated sample results associated with non-compliant calibrations.

Field Duplicates

Were field duplicates submitted for radio chemical analysis at a frequency of 1 per 20 field samples per matrix and per method?	_____	_____	_____
Do solid sample field duplicate results have a relative percent difference of less than or equal to 50% when the target is detected in both field samples at levels greater than 5 times the MDC or is the mean difference between field duplicate results $\leq$ 3 when one or both field duplicate samples exhibit a concentration forthe target that is less than or equal to 5 times the MDC?	_____	_____	_____

ACTION: If any of the criteria described above are not met, both results reported for the field duplicate pair are qualified “J” estimated.